

Investigating Band Structure Modifications in 2D Materials and Heterostructures via Scanning Tunneling Microscopy and Spectroscopy

by

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Declaration of Authorship

I declare that this thesis and the works presented in it are entirely my own. I am aware of the University of Ottawa's regulations concerning plagiarism. Parts of this work have been published before, in particular, some of the contents of Chapter 2, and Appendices 8.1, 8.2, 8.3 (except 8.3.1), 8.4, and 8.5, were previously included in my own MSc thesis[1], and some of Chapters 4 and 5 have been published before, the contents of which have been repeated here with some modifications. Where I have consulted or used the published work of others, this is properly acknowledged through citations in the text. For each chapter in this thesis, the contributions of myself and others are stated below.

Chapter 3: Ryan Plumadore (R.P.) envisioned the idea for this work, based largely on [2] Lupke et al., ”*Proximity-induced superconducting gap in the quantum spin Hall edge state of monolayer WTe_2* ”, Nat. Phys., **16**(5), 526–530 (2020). R.P. and Justin Boddison-Chouinard (J.B.-C.) developed and tested the procedure.

Chapter 4: The WSe_2 experiments were suggested by Adina Luican-Mayer (A.L.-M.). R.P. prepared the samples and performed the experiments. R.P. and J.B.-C. analyzed the data.

For the ReS_2 , A.L.-M. and Gregory Lopinski (G.L.) proposed the experiments. R.P. prepared the samples with help from J.B.-C., and R.P. performed the experiments. R.P. analyzed the data. Mohsen Modarresi (M.M.), Pawel Potasz (P.P.), and Pawel Hawrylak (P.H.) are responsible for the density of states calculations. Mehmet Baskurt (M.B.), Hasan Sahin (H.S.), and Francois M. Peeters (F.M.P.) are responsible for all other calculated data. The manuscript[3] was written by A.L.-M. and R.P., and edited by all authors listed in this paragraph.

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Al Ezzi (M.M.A.E.) and Shaffique Adam (S.A.) are responsible for all simulated or calculated data. R.P. and A.L.-M. wrote the manuscript[4], which was edited by all authors listed.

Chapter 6: A.L.-M. and Zhiqiang Mao (Z.M.) envisioned the idea for this work. R.P. prepared the samples. R.P. and Leena Aggarwal (L.A.) performed the experiments and analyzed the data. R.P. wrote the first draft of the manuscript (in preparation), which was edited with L.A. and A.L.-M.'s help. Yanglin Zhu (Y.Z.), and Yingdong Guan (Y.G.) grew and provided the MnBi_2Te_4 .

Abstract

This thesis explores structural and electronic properties of 2D crystals and van der Waals heterostructures (vdWH) at the nanometre scale. In particular, the experiments presented characterize modifications to the local density of states induced by defects, moiré potentials, or by disrupted topological order of surface states. Such structures can be utilized as part of a platform to explore physics phenomena by tuning interlayer interactions, which can lead to emergent properties previously only accessible in more complicated systems. Bulk 2D crystals are explored using scanning-probe techniques, with the intent of learning and applying their characteristics to tailored van der Waals heterostructures. Room temperature and low temperature ultrahigh vacuum scanning probe microscopy (scanning tunneling microscopy and spectroscopy) is used as the primary characterization method.

The main results in this thesis are: (a) observations and characterization of the local lattice defects in bulk semiconducting transition metal dichalcogenides (TMDs) by scanning tunneling microscopy and spectroscopy (STM/S), (b) the development of a fabrication technique for creating atomically clean van der Waals heterostructures, (c) an example of such a device through STM/S measurement of a graphene-rhenium disulfide heterostructure, and (d) scanning tunneling microscopy and spectroscopy study of bulk crystals of antiferromagnetic topological insulator, MnBi_2Te_4 , where the spatial heterogeneity of the spectroscopic features are investigated.

Altogether, these results establish groundwork for building more complex heterostructures which are suitable for scanning probe experiments and assist in exploring fundamental physics phenomena through the moiré framework.

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List of Publications

Note: from the list below, items 1, 5, and 6 are included in this thesis.

1. **Ryan Plumadore**, Leena Aggarwal, Yanglin Zhu, Yingdong Guan, Zhiqiang Mao, Adina Luican-Mayer. *Visualizing the heterogeneity of the surface and edge states in magnetic topological insulator $MnBi_2Te_4$* . In preparation.
2. Laurent Molino, Leena Aggarwal, Indrajit Maity, **Ryan Plumadore**, Johannes Lischner, Adina Luican-Mayer. *Influence of atomic relaxations on the moiré flat band wavefunctions in antiparallel twisted bilayer WS_2* . (2023) Nano Lett. 23, 24, 11778-11784
3. Sergio Ramos, Bruno Carvalho, Raphael Longuinhos Monteiro Lobato, Jenaina Ribeiro-Soares, Cristiano Fantini, Henrique Ribeiro, Laurent Molino, **Ryan Plumadore**, Tony Heinz, Adina Luican-Mayer, Marcos Pimenta *Selective electron-phonon coupling in dimerized 1T-TaS₂ revealed by resonance Raman spectroscopy*. (2023) ACS Nano. 17, 16, 15883–15892.
4. Laurent Molino, Leena Aggarwal, Vladimir Enaldiev, **Ryan Plumadore**, Vladimir Falko, Adina Luican-Mayer. *Ferroelectric switching at symmetry-broken interfaces by local control of dislocation networks*. (2023) Adv. Mater. 2207816
5. **Ryan Plumadore**, Mehmet Baskurt, Justin Boddison-Chouinard, Gregory Lopinski, Mohsen Modarresi, Pawel Potasz, Pawel Hawrylak, Hasan Sahin, Francois M. Peeters, and Adina Luican-Mayer. *Prevalence of oxygen defects in an in-plane anisotropic transition metal dichalcogenide*. (2020) Phys. Rev. B. 102, 205408
6. **Ryan Plumadore**, Mohammed M. Al Ezzi, Shaffique Adam and Adina Luican-Mayer.

- Moiré patterns in graphene–rhenium disulfide vertical heterostructures.* (2020) Journal of Applied Physics 128, 044303
7. Ranjana Rautela, Samantha Scarfe, Jean-Michel Guay, Petr Lazar, Martin Pykal, Saied Azimi, Cedric Grenapin, Justin Boddison-Chouinard, Alexei Halpin, Weixiang Wang, Lukasz Andrzejewski, **Ryan Plumadore**, Jeongwon Park, Jean-Michel Ménard, Michal Otyepka, and Adina Luican-Mayer. *Mechanistic Insight into the Limiting Factors of Graphene-Based Environmental Sensors* (2020) ACS Appl. Mater. Interfaces, 12, 35, 39764–39771
8. Sergio L.L.M. Ramos, **Ryan Plumadore**, Justin Boddison-Chouinard, Saw Wai Hla, Jeffrey R. Guest, Dave Gosztola, Marcos A. Pimenta, Adina Luican-Mayer. *Suppression of the commensurate charge density wave phase in ultrathin 1T-TaS₂ evidenced by Raman hyperspectral analysis.* (2019) Phys. Rev. B 100, 165414
9. Justin Boddison-Chouinard, **Ryan Plumadore**, Adina Luican-Mayer. *Fabricating van der Waals Heterostructures with Precise Rotational Alignment.* (2019) J. Vis. Exp. (149), e59727

List of Abbreviations

Abbreviation	Definition	Page
2D	Two-dimensional	<i>v</i>
AC	Alternating Current	23
ARPES	Angle-Resolved Photoemission Spectroscopy	70
AFM	Atomic Force Microscopy	35
BP	Black Phosphorus	7
CB	Conduction Band	65
DC	Direct Current	23
DFT	Density Functional Theory	53
DOS	Density of States	18
EBL	Electron-Beam Lithography	138
hBN	hexagonal Boron Nitride	5
IGS	In-Gap States	46
IPA	Isopropyl Alcohol	146 (3)
LDOS	Local Density of States	49
LT	Low Temperature	29
PDMS	Polydimethylsiloxane	37
PDOS	Partial Density of States	49
PID	Proportional–integral–derivative	131
PL	Photoluminescence	5
PMMA	Poly(methyl methacrylate)	34
PPC	polypropylene carbonate	37
PVA	Polyvinyl Acetate	34
SOP	Standard Operating Procedure	24
RT	Room Temperature	29
SEM	Scanning Electron Microscopy	137
STM	Scanning Tunneling Microscopy	<i>v</i>
STS	Scanning Tunneling Spectroscopy	<i>v</i>
TEM	Transmission Electron Microscopy	46
TI	Topological Insulator	7
TMD	Transition Metal Dichalcogenide	<i>v</i>
TSP	Titanium Sublimation Pump	26
QAH	Quantum Anomalous Hall	2
UHV	Ultrahigh Vacuum	25
VB	Valence Band	50
vdWH	van der Waals Heterostructure	<i>v</i>
XPS	X-ray Photoelectron Spectroscopy	42

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Chapter 1

Introduction

Since the simple exfoliation of graphene was demonstrated in 2004 [5], and with the same on transition metal dichalcogenides (TMDs) following shortly after[6], the popularity of 2D materials research has grown at an accelerating pace. Earlier efforts with devices assembled from 2D materials focused on utilizing properties present in their constituent layers, assembling them as components of van der Waals heterostructures (vdWH). Such devices can enhance the intrinsic properties of their constituent layers, or be arranged in particular ways to yield properties not present in the separate layers. Indeed, in recent years experimental developments have shown engineering of 2D materials properties within the heterostructure scheme to be more complex, especially with regards to the emerging effects of moiré patterns[7, 8]. For instance, long-lived moiré excitons may host topologically nontrivial flat bands [9–11], while peculiar transport properties arise in small-angle twisted heterostructures[12–21]. Solitons and domain walls with complex behaviours can emerge as a result of local atomic reconstructions, affecting structural[22–24], mechanical[25, 26], and electronic properties[27, 28]. Flat band engineering has dominated the graphene heterostructure landscape, and that focus has begun shifting towards TMDs and other 2D materials of late.

Layered Materials. A defining characteristic 2D materials share is their weak inter-layer van der Waals bonding. Through mechanical exfoliation, this property allows them to be reduced to 2D layers. Outside of this commonality, the types of 2D materials are vast,

including semiconductors [29–32], metals[33, 34], superconductors[35, 36], insulators[37], and more[38–42]. Among 2D materials are the transition metal dichalcogenides, a family of materials with the chemical formula MX_2 , where a transition metal ($M = \text{Mo, W, Re, etc...}$) is sandwiched between two layers of chalcogens ($X = \text{S, Se, Te}$). The most studied are the group VI TMDs which exist in the semiconducting 2H-phase, where the atoms are covalently bonded in-plane and arranged in a honeycomb lattice alternating at each site between metal and chalcogen atoms. Other stable phases can be made by intercalating metals into the lattice[43] or by doping with transition metals from other groups[44]. Generally, the structural and electronic properties are governed by the group of the transition metal, in other words, the number of d -orbital electrons. For example, group VII TMDs have an additional electron on each metal atom when compared to group VI TMDs, a change that is sufficient to induce a Peierls distortion, reconstructing the lattice into a series of parallel chains of diamond-shaped clusters.

As mentioned above, these materials can all be reduced from bulk crystals to the monolayer limit via mechanical exfoliation. In TMDs this breaks the inversion symmetry, modifying the electronic properties of the materials. For example, the *2H*-phase is reduced to *1H*, and in 2D semiconductors this induces a transition from indirect to direct band gaps. Inversion symmetry can have important consequences on properties of some layered materials, allowing quantum anomalous Hall (QAH) effects, or determining the magnetic order for certain layer parities[45–47].

van der Waals heterostructures. When multiple layers of different 2D materials are stacked vertically, the resulting devices are called van der Waals heterostructures. Inter-layer interactions between adjacent layers can have consequences on the device properties, sometimes leading to unexpected behaviours in structurally simple systems. Initial efforts in vdWH samples focused on enhancing the useful properties of a given layer within the device.

A prominent result in the vdWH field was the experimental realization of flat bands in magic angle graphene, where two monolayers of graphene were rotated and stacked to form a correlated insulator. But when rotated at a specific angle and tuned such that there are two electrons per unit cell, the system undergoes a transition from insulating to superconducting behaviour. MIT Professor Pablo Jarillo-Herrero, speaking at the 2022 Dresselhaus Lecture, reflected on the impact of the discovery of magic angle graphene:

“Moiré quantum matter has meant the merging of several modern condensed matter physics communities – 2D van der Waals materials and heterostructures, strongly correlated materials, and topological condensed matter physics. All of these types of physics and systems come together in moiré quantum matter.”

This newfound realization of the possibilities with 2D material devices stimulated interest for a more systematic and thorough characterization of the myriad combinations that can be achieved with van der Waals heterostructures (vdWH). Indeed, vdWHs have provided a new platform to investigate quantum materials, starting from relatively simple components.

Band Engineering via Defects. Atomic scale defects in semiconductors enable their technological applications and the realization of novel quantum states. Being semiconductors, defects play an important role in both the local electronic properties and the behaviour of devices assembled from such materials. Lattice imperfections modulate the electronic characteristics of the material, which can introduce localized electronic energy states within the semiconductor’s band gap[48]. These energy levels can be occupied by electrons, with a probability determined by the Fermi distribution, for a given temperature T ,

$$f(E) = \frac{1}{e^{(E-E_F)/k_b T} + 1} \quad (1.1)$$

with E_F the Fermi level and k_b the Boltzmann constant. The distribution of electrons in the

conduction band is then given by,

$$n(E) = N_C(E)f(E) \quad (1.2)$$

where N_C is the density of states in the conduction band. Similarly, with N_V the density of states in the valence band, the distribution of holes in the valence band is,

$$p(E) = N_V(1 - f(E)) \quad (1.3)$$

In an intrinsic semiconductor, the concentration of electrons in the conduction band (n_i) should be equal to the concentration of holes in the valence band ($p_i = n_i$), and the intrinsic Fermi energy, E_{F_i} , should be near the middle of the bandgap. But in extrinsic semiconductors, where dopants or impurities are added into the lattice, the distribution of electrons and holes in the material changes. Since the Fermi energy is related to the distribution function, it will also shift away from its intrinsic level. This process alters the electrical characteristics of the semiconductor, and the electron and hole concentrations are now given by:

$$n_0 = n_i \exp\left(\frac{E_F - E_{F_i}}{k_b T}\right) \quad (1.4)$$

$$p_0 = n_i \exp\left(\frac{E_{F_i} - E_F}{k_b T}\right) \quad (1.5)$$

The position of the Fermi level can be determined as a function of the doping concentration and temperature (with E_C the energy of the conduction band),

$$E_F = E_C - k_b T \ln\left(\frac{N_C}{n_0}\right) \quad (1.6)$$

In TMDs, defects in the first monolayer can act as nucleation sites for subsequent layers, leading to a wider range of orientations[49]. Defect states in twisted WS_2 homolayers are

believed to act as exciton trapping sites, exhibiting ordered splitting with a narrow full-width at half-maximum, yet photoluminescence (PL) studies cannot reveal which of the defects in particular may contribute such states[50]. In CrI_3 , the intrinsic 2D ferromagnetism may lead to the formation of magnetic topological defects, a prerequisite for the excitonic anomalous Hall effect[51], while in $\text{MnBi}_6\text{Te}_{10}$, the defects may facilitate tunable magnetic topological order[52]. The optical and electrical properties of TMDs make them attractive materials for solar energy conversion and electrocatalysis applications, yet these applications depend on the defects in the layers to drive reactions[53, 54]. PL measurements of WS_2 have found a strong inverse relationship between defect density and PL intensity[55]. A well-balanced defect concentration in tungsten TMDs was shown to optimize its adsorption and catalytic abilities, enhancing the cathodic process in lithium-sulfur batteries[56].

With the changes caused by defects varying from material to material, the first question this thesis will aim to answer is on the nature of defects in some specific semiconducting 2D TMDs. If understood, the effect of such point defects could be utilized for band engineering, spintronics, and in general to influence device properties in interesting ways[57]. Understanding the properties of the intrinsic defects in TMDs can guide efforts to engineer their behaviour for specific photovoltaic and catalytic applications, as solid-state platforms for quantum dot qubits, single photon emitters, or other topological quantum phases[52, 58].

Band Engineering via Moiré Patterns. Heterostructures of atomically thin two-dimensional materials offer a playground for realizing physical systems with properties that are finely tuned by interlayer interactions[59]. Examples include the presence of correlated states in moiré patterns of twisted graphene layers[60–65], observation of Hofstadter butterfly in twisted graphene/hexagonal boron nitride (hBN) layers[66], or superconductivity induced in the edge states of a quantum spin Hall insulator[2].

Geometric models can be used to determine the Moiré lattice in real space[67], but the re-

sulting Moiré patterns act as a periodic potential which can modify the electronic structure of the system[68]. For instance, the density of states of graphene has long been understood[69]. The tight-binding model can be used to derive the Hamiltonian[70], from which we can find that the energy bands near the Dirac points follow a linear dispersion relation,

$$E = \hbar v_f k \quad (1.7)$$

where v_f is the Fermi velocity, and k the wavenumber. From there we can derive the density of states, with spin and valley (K and K') degrees of freedom,

$$N(k)dk = 2 \times 2 \times \frac{2\pi k dk}{\left(\frac{2\pi}{L_x}\right)\left(\frac{2\pi}{L_y}\right)} \quad (1.8)$$

Using $kdk = EdE/(\hbar v_f)^2$ and taking the density of states per unit area, $A = L_x L_y$, we obtain,

$$g(E) = \frac{2E}{\pi \hbar^2 v_f^2} \quad (1.9)$$

This tells us that the energy bands in graphene form Dirac cones, which meet at the Dirac points where the energy is linear in momentum. In this relatively simple system, periodic modulations brought about in vdWH by Moiré bands can be leveraged for band engineering[71–73]. For example, in twisted bilayer graphene, just as the physical lattices of the two layers are rotated, the K points in the first Brillouin zone of the two graphene layers are rotated from each other[74]. This leads to the formation of a new, smaller Brillouin zone, which is the manifestation in the reciprocal space of the much larger Moiré superlattice in real space. It is from this smaller Brillouin zone that, following a continuum model, the so-called magic angles which lead to vanishing Fermi velocity, and hence flat bands, can be

found[75, 76]. Another example is the use of different lattice symmetries in vdWH, as will be explored later in Chapter 5, which, for example, could be used to apply Kronig-Penney type 1D periodic potentials. The resulting anisotropic Dirac cones in graphene would preserve the linear dispersion relation found above, but are renormalized in k_x and k_y directions such that the group velocities in particles moving perpendicular to the periodic direction is reduced, whereas those moving along the potential are unaffected[77].

Studies of graphene placed on semiconducting TMDs[78] revealed that such a substrate can provide improved screening and reduced scattering. Different types of periodic inter-layer interactions resulting from heterostructures where graphene is layered with in-plane anisotropic TMDs have recently been explored using substrates such as ReSe₂[79] or BP[15]. On BP, it was reported to give rise to shear-strained superlattices resulting in pseudo-magnetic fields. For the case of graphene/ReSe₂ interfaces[79], twist-dependent moiré patterns were measured using scanning tunneling microscopy. These studies motivate further development and understanding of intricate moiré patterns formed at interfaces between crystals with distinct symmetries. Scanning tunneling microscopy and spectroscopy (STM/STS) are experimental techniques well-equipped to offer such insight, as they can visualize the structure and its heterogeneity at the atomic scale as well as give information about the electronic states of the system.

Band Engineering via Topology. Topological insulators (TIs) are electronic materials which have an insulating band gap in the bulk, while hosting robust conducting states at their edges or surfaces, protected by time-reversal symmetry[80–86]. Mathematically, topological materials are those which can be characterized by a non-zero topological invariant, the simplest of which is the Chern number in two-dimensional topological systems. The derivation of this number and its consequences are intricately related to the mathematics of Berry phases and curvature (see Chapter 3 of [87], or [88–91]), but such derivations are

outside the scope of this thesis. The important result is that TIs are characterized by two properties: (i) gapless boundary states, which are robust against perturbations, which leads to the second property, that (ii) a boundary between a TI and a topological trivial material always exhibits gapless states[92].

In magnetic topological insulators, the intrinsic combination of properties opened a burgeoning arena for the discovery of novel phenomena such as the quantum anomalous Hall effect and the chiral Majorana edge states[92–98]. The introduction of magnetism to the topological system breaks the time-reversal symmetry which protects the surface states. Thus, in a magnetic topological insulator, the surface Dirac fermions become massive under the presence of the magnetic field, and a gap opens at the Dirac point. Introducing ferromagnetic order to a topological insulator preserves the bulk electronic gap while gapping the spin-momentum locked Dirac-like surface states, producing dissipationless edge modes[93].

The first experimental realization of magnetic topological insulators followed the strategy of chemical doping of thin TI films with magnetic 3d transition-metal elements [94, 95], gapping out the surface states near the Dirac point. Topologically nontrivial gaps greater than 100meV have been observed, for example in Gd-substituted Bi_2Te_3 [99], while others have shown that the gapless nature of the surface states can be preserved even in the presence of magnetic impurities [100]. Yet, such systems have an inherently inhomogeneous distribution of magnetic impurities across the surface, which can present a challenge when searching for novel topological phases. Thus, direct evidence of the topological nature of the gapped surfaces remained elusive[101].

Surface and Interface Characterization with Scanning Probe Techniques. Characterization of the nanoscale variations in 2D materials and devices is essential to understanding their properties. Fabrication of devices incorporating semiconducting layered materials can be achieved through a variety of techniques, yet a robust understanding of the local

electrostatic behaviours induced by defects is needed in order to steer decisions on future devices. The influence of defects are expected to be spatially localised at the nanoscale around neighbouring defects[102], and their distribution across the surface is not always homogeneous, traits which challenge the spatial resolution and sensitivity of many characterization techniques[103, 104]. Likewise for vdWH, due to local variations in the rotation angle, their emergent properties can fluctuate across the typical length scale of a device. Since it is a direct result of the interlayer interaction strength, the intensity of the moiré patterns can vary strongly across these length scales as well.

On the other hand, scanning probe techniques are of particular use for 2D materials and vdWH, where the entire sample is a surface. Scanning probe techniques, for example scanning tunneling microscopy and spectroscopy can be used to probe the structure and electronic properties of surfaces. This measurement technique involves an atomically sharp tip positioned close enough to a conducting surface to allow a quantum mechanical tunneling current to flow, which is then used to image the surface structure and measure its local electronic states with atomic scale resolution. It can directly visualize these nanoscale features and provide insight into the ways they may affect the local density of states. Optical or electronic transport techniques, which average over the bulk of the material, may not observe behaviour localized to the surface [105]. As STM measures only local information, it is thus a desirable method to characterize layered materials, being uniquely adapted to search for and study effects of impurities, defects, and moiré patterns. Chapter 2 will describe in more detail the physical principles and experimental details of scanning tunneling microscopy.

Despite the utility of STM for characterization of 2D materials, it imposes additional constraints on the fabrication of devices. Typical device fabrication involves the top-down assembly of layers through the use of polymers to pick up and place subsequent layers. These polymers leave contamination on the surface of the device, which can be difficult to remove

and can interfere with surface probe techniques. This issue can be averted in samples where the measurement technique will not require direct access to the surface, or where the surface condition is less critical (e.g. optical or transport measurements) by capping the entire heterostructure, most commonly with the insulating 2D material hexagonal boron nitride. It is crucial for interfaces and surfaces to be free of contaminants for STM experiments, yet this solution of encapsulating devices evidently renders the sample inaccessible to scanning probe techniques. Thus, a fabrication technique named the “inverted dry-transfer method” was developed, described in Chapter 3, which maintains pristine surfaces and allows direct access to the surface.

In Chapter 4, characterization and analysis of the atomic defects imaged in two TMDs are presented, namely, WSe_2 and ReS_2 . In the first case, for the semiconducting WSe_2 , we are interested in the distribution of defects on the surface. We characterize the defect density to understand the potential impact on quantum devices made from this material. Further, spectroscopy data is acquired which can be used to infer the nature of the defects in this material. For ReS_2 , we use scanning tunneling microscopy and spectroscopy complemented by ab-initio calculations to determine the nature of defects in this anisotropic van der Waals layered semiconductor. The presence of lattice defects is revealed and by comparison of their topographic and spectroscopic signatures with ab initio calculations, their origin is determined as oxygen atoms adsorbed at lattice point defect sites. The results of both of these data sets provide an atomic-scale view into the semiconducting transition metal dichalcogenides, paving the way toward understanding and engineering their properties at large.

A second theme explored through this thesis is the fabrication and characterization of van der Waals heterostructure devices for STM. As mentioned above, the inverted dry-transfer method was developed to allow fabrication of atomically clean vdWH for STM experiments.

As an example of a heterostructure made by means of this technique, results are presented in Chapter 5 of a device where monolayer graphene was placed on bulk ReS_2 . Challenges include the fabrication of devices with clean surfaces, and tailoring semiconductor devices for low temperature measurements, both of which can be addressed by adapting the inverted dry-transfer technique at specific steps.

Chapter 6 presents results on the characterization of a bulk MnBi_2Te_4 crystal. MnBi_2Te_4 is a topological insulator with intrinsic antiferromagnetism, a combination of properties which is anticipated to lead to non-trivial gapped surface states in the TI, without the usual magnetic inhomogeneity present in doped TI samples. However, there is disagreement in the literature on the origin and even the presence of the gap in MnBi_2Te_4 . Scanning tunneling spectroscopy is used to conclusively reveal the presence of a band gap, while exploration of the band structure at many separate areas on MnBi_2Te_4 crystals provides insight into the dilemma and helps guide future implementation of this material in devices which could exploit its unique properties.

Chapter 2

Scanning Tunneling Microscopy

This chapter describes the primary experimental tool used for characterization of samples in this thesis, the scanning tunneling microscope, an invention which awarded the 1986 Nobel Prize in Physics to its creators, Gerd Binnig and Heinrich Rohrer.[106] In STM, an atomically sharp metallic tip and a conductive surface are brought close enough to allow a quantum mechanical tunneling current to flow between them under an applied voltage bias. By utilizing quantum mechanical tunneling, STM collects topographic and electronic information about the surfaces of samples at the atomic level.

In an STM experiment, depending on the polarity of the sample bias, electrons flow from the tip to the sample (positive) or from the sample to the tip (negative). In other words, scans acquired with positive bias generate an empty state image, while a negative bias scan will generate a filled state image of the sample. In the most common operation mode, the tunneling current is kept constant with a feedback loop. By recording the change in tip height at each point (x, y) along the surface, an array is generated which represents a contour plot of the surface (z) . If the tunneling current increases, the tip height is increased, and vice versa. Since STM measures on a subnanometre length scale, we find ourselves with a capable tool for characterizing 2D materials that consist entirely of a surface with a definite lattice, and for investigating the interesting features which appear at those surfaces such as defects, edge states, moiré patterns, and local surface reconstructions.

A crucial aspect of this technique is the mitigation of all sources of noise, and along with this an understanding of the spatial and energy resolution limits of the system. In this chapter, we will first understand the principle of STM by deriving the tunneling equation with some simple assumptions. From there, we shall determine the limits of our resolution for topography and spectroscopy. These principles are applicable to any system, and so the next section will provide specific details about the instrumentation used in these experiments. Finally, the chapter will conclude with a description of some key experimental techniques, including the inverted dry-transfer fabrication technique by which atomically clean van der Waals heterostructures are prepared for STM.

2.1 Principle of STM

The physical principle of STM can be represented by a simple one-dimensional system analogous to the tip-sample barrier. The Bardeen Formalism, presented below, describes tunneling phenomena in general, and Tersoff and Hamann's model described later in this section applied this solution specifically to STM tunneling.

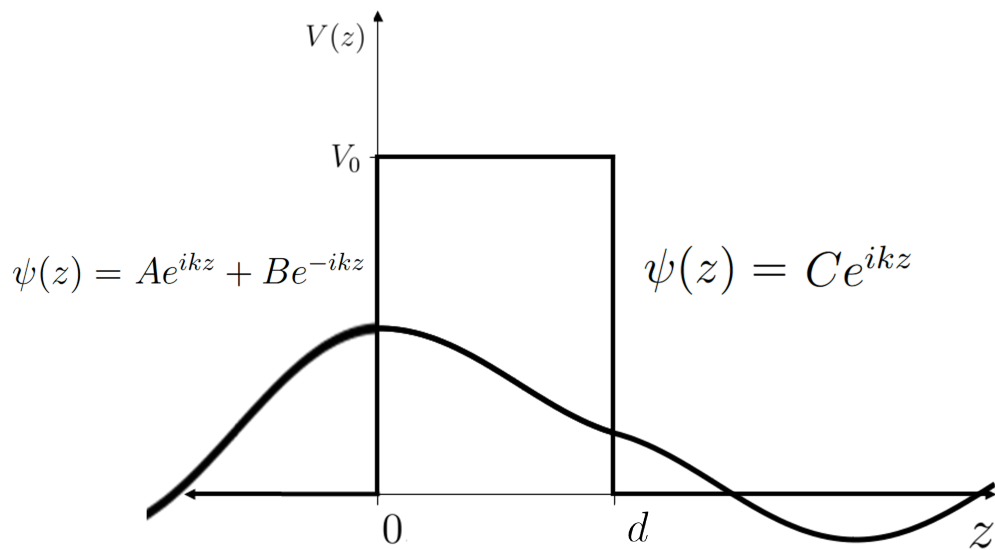


Figure 2.1: A one-dimensional rectangular barrier of height V_0 and width d .

Tunneling. Taking the simplified view of a one-dimensional barrier, represented schematically in Figure 2.1, assume we have a potential of height V_0 and width d . This potential acts as a barrier to the flow of electrons, which we can approximate as a barrier between two metal electrodes. For an incident wave with solutions $\psi(z)$, we will be able to solve for the transmission coefficient. By solving a system of equations described by the solutions inside and outside the potential (Appendix 8.1), we find[107] (with $K = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$):

$$T = \frac{|C|^2}{|A|^2} \approx \frac{16E(V_0 - E)}{V_0^2} e^{-2Kd} \quad (2.1)$$

for electrons with energy E tunneling through a barrier potential V_0 of width (tip-sample separation) d . The tunneling current is proportional to this transmission coefficient, which has an exponential decay in the barrier width:

$$I_t \propto e^{-2Kd} \quad (2.2)$$

and is thus extremely sensitive to the distance between the sample and tip, d . In practice, this exponential relationship is used to measure the topography of samples by maintaining a constant tunneling current during measurements. A feedback loop adjusts the tip height while scanning, resulting in a contour map of the surface as the tip scans along. This is the most common mode used to obtain topographic information in STM.

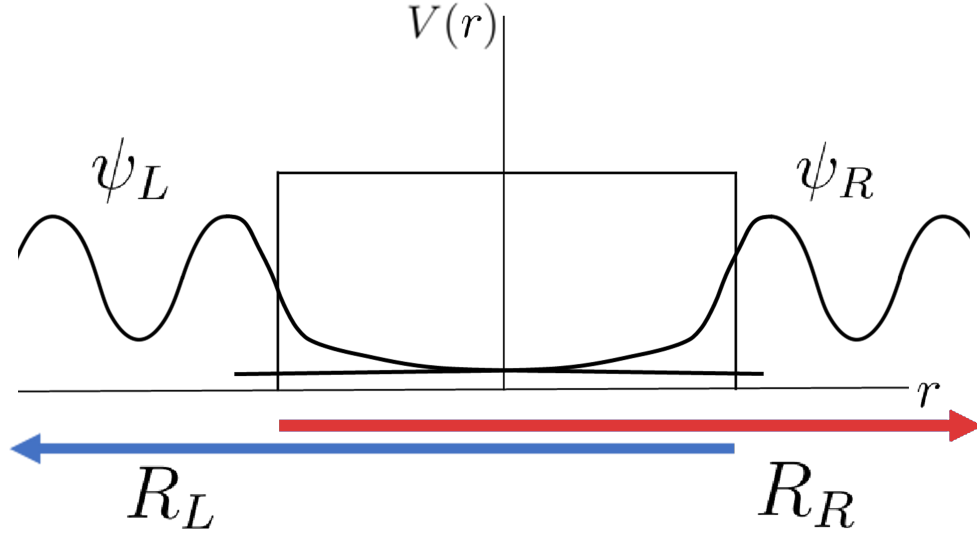


Figure 2.2: Separated system of Bardeen's Formalism[108, 109].

Bardeen Formalism. Tunneling can be more precisely described by using the Bardeen formalism[108]. This is a many-particle approach which can be extended to describe tunneling phenomena, including STM tunneling. The basis of the formalism is to separate the system into two subsystems[109, 110] with known Hamiltonians, H_L and H_R , for the left (R_L) and right (R_R) regions, as well as a “transfer” Hamiltonian, H_T , for the overlapping region in the middle.

The wave functions describing the left and right subsystems are $\psi_{L,i}(\vec{r})$ and $\psi_{R,i}(\vec{r})$. The rate of electron transfer can be found from the Fermi golden rule[111], by considering the probability P of an electron to tunnel from the state $\psi_{L,0}$ to $\psi_{R,n}$:

$$P = \frac{2\pi}{\hbar} \sum_n \left| \langle \psi_{R,n} | H_R + H_T | \psi_{L,0} \rangle \right|^2 \delta(E_{R,n} - E_{L,0}) \quad (2.3)$$

Here the portion $\langle \psi_{R,n} | H_R + H_T | \psi_{L,0} \rangle$ is the tunneling matrix element, or M . The matrix

element can be represented as:

$$M = \int_{-\infty}^{\infty} \psi_{R,n}^{\dagger} (H_R + H_T) \psi_{L,0} \, d\vec{r} \quad (2.4)$$

Solving for M is difficult because the full Hamiltonian is not known. Bardeen's approach is to assume the Hamiltonian can be described by considering only H_L in R_L , and H_R in R_R . Since $\psi_{L,i}(\vec{r})$ decays across the barrier and is approximately zero in R_R , the assumption is that $H \cong H_R$ in that region. Similarly, $H \approx H_L$ in R_L . If we consider the integral in M over a surface separating R_L and R_R , it can be reformulated as a surface integral:

$$M = \frac{\hbar^2}{2m} \int \psi_{L,0} \nabla \psi_{R,n}^{\dagger} - \psi_{R,n}^{\dagger} \nabla \psi_{L,0} \, dS \quad (2.5)$$

The tunneling matrix element can now be calculated with only the wavefunctions $\psi_{L,0}(\vec{r})$ and $\psi_{R,n}(\vec{r})$. In applying this formalism to STM, we are hindered by the fact that the atomic structure of the tip, and therefore $\psi_{L,0}$, is not known in general. If we can solve for M through some simplifying assumptions, then we can calculate the transmission coefficient in equation 2.3.

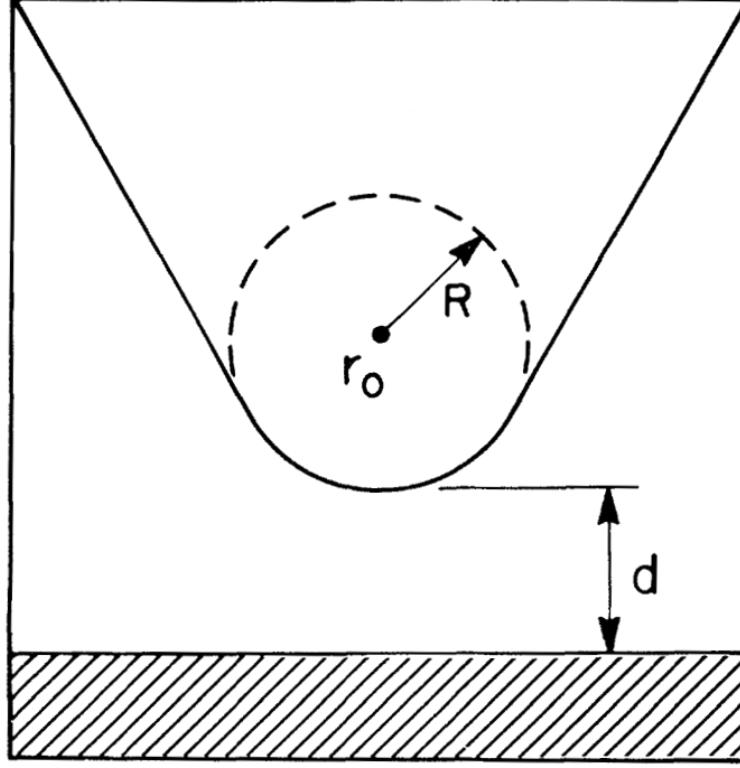
***s*-wave-tip model.**

Figure 2.3: Schematic picture of tunneling geometry in the *s*-wave model. The shape of the tip is arbitrary, but is assumed to be locally spherical with radius of curvature R at its nearest point to the surface. Centre of curvature is r_0 , and the shaded region represents the sample[112, 113].

The first theory to apply the Bardeen formalism to STM was presented in 1985 by Tersoff and Hamann[112, 113]. The tip is described by the simplest terms possible, as seen in Figure 2.3. In this theory, the sample will be weakly coupled to the tip, and tunneling will be mainly from tip states in the *s*-wave orbital (ignoring any angle dependent contributions). Perturbation theory is therefore suitable to solve for the junction. An expression can be obtained for the current which is independent of tip contributions[110, 114, 115].

$$I = \frac{4\pi e}{\hbar} \int_{-\infty}^{\infty} \left[f(E_F - eV + \epsilon) - f(E_F + \epsilon) \right] \times \rho_{R,n}(E_F - eV + \epsilon) \rho_{L,0}(E_F + \epsilon) |M|^2 d\epsilon \quad (2.6)$$

where $f(E)$ is the Fermi distribution function, E_F the Fermi level, V is the effective local potential barrier height, and $\rho_{L,0}(E_F)$ is the density of states (DOS) of the tip at the Fermi level. The sample's DOS at the Fermi level is the remaining portion of the above expression:

$$\rho_{R,n}(E_F, r_0) = \sum_n \left| \Psi_n(r_0) \right|^2 \delta(E_{R,n} - E_F) \quad (2.7)$$

Since the wave functions decay exponentially in the z -direction, we get an expression relating this DOS to the distance to the sample, d , and the radius of the tip, R :

$$\Psi_n(r) \propto \exp(-\chi z) \implies \left| \Psi_n(r_0) \right|^2 \propto \exp(-2\chi(d + R)) \quad (2.8)$$

The validity of this expression hinges on the assumption that the s -wave contributions from the tip are the most significant in STM tunneling. This has been shown to be true for most cases with free-electron model tips[113, 116–118], except in the case of tunneling to band-edge states[119].

Spectroscopy. Equation 2.8 demonstrated again the exponential dependence of the tunneling current on the tip-sample separation. In equation 2.6, one can observe that the current is also proportional to the sample's DOS (equation 2.7).

In the limit of low temperature and small bias voltage, this expression for the current can be simplified, as $f(E)$ becomes a step function. In practice, this is the case as long as the energy resolution is greater than $k_B T$. By expressing M in terms of a current density operator and assuming it can be described by a step function as well, $|M|^2$ will be roughly constant within the region of interest[108]. In that case we can collect all the constants from the integral in equation 2.6, and we get:

$$I \propto \int_0^{eV} \rho_{R,n}(E_F - eV + \epsilon) \rho_{L,0}(E_f + \epsilon) d\epsilon \quad (2.9)$$

This expression tells us that the DOS of the tip and sample are equally significant in the tunneling current. To measure the states in the sample, we need to eliminate $\rho_{L,0}$ from the integral. This is done experimentally by choosing tips made of metals which obey the free-electron model (typically transition metals, e.g. tungsten). In that case their DOS will be constant over the range of energies we are interested in, and we are left with:

$$I \propto \int_0^{eV} \rho_{R,n}(E_F - eV + \epsilon) d\epsilon \implies \frac{dI}{dV} \propto \rho_{R,n}(E_F - eV) \quad (2.10)$$

This is applied in scanning tunneling spectroscopy (STS) by measuring the derivative of the current ($\frac{dI}{dV}$) while running through a range of bias voltage (V_b) values, and thus providing a direct measurement of the local DOS at each energy value.

2.2 Resolution in STM measurements

2.2.1 Lateral Resolution

When moving the tip laterally across the surface, a feedback loop adjusts the tip-sample separation to keep the current constant. The exponential dependence of the tunneling current provides a resolution on the order of picometres, provided the experimental conditions (noise, surface and tip condition, etc) are stable. An assumption we made in our derivation earlier is that the tunneling current flows from the atom or atoms at the apex of the tip, a behaviour which also implies a high lateral resolution. In order to calculate the lateral resolution, we need only our understanding of the working principle of STM from Tersoff and Hamann's model. Consider the simple schematic shown in Figure 2.4. We know the current directly under the tip apex is given by:

$$I \propto e^{-2Kz} \quad (2.11)$$

where $K = \frac{\sqrt{2m}}{\hbar} \sqrt{V_0 - E}$, and z is the distance from the tip apex to the sample surface.

If we consider a point which is not directly under the tip apex, but laterally displaced by some amount Δx , then the tip height at this point will be greater by an amount $\Delta z = R - \sqrt{R^2 - (\Delta x)^2}$. This means the contribution to the current from this point becomes:

$$I \propto e^{-2K(z+\Delta z)} \quad (2.12)$$

and the change in height leads to a reduced current measured from this nearby location. It is straightforward now to calculate the resolution. Assume a typical tip-sample distance of $6\text{\AA}$, $K \cong 1$, and a tip radius of $9\text{\AA}$ (corresponding to the approximate radius of the s -wave tip state). Then, for a lateral translation of $\Delta x \cong 4\text{\AA}$, equating to a change in height of only $\Delta z \cong 1\text{\AA}$, the tunneling current is reduced by an order of magnitude. This lateral translation defines a column of width $2\Delta x < 1\text{ nm}$, which consequently is the lateral resolution limit of the STM.

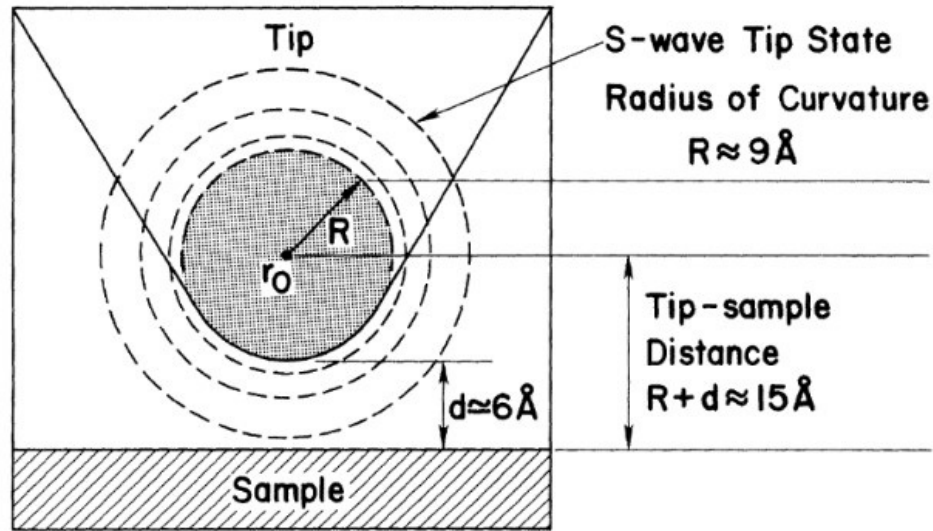


Figure 2.4: Schematic representation of the s -wave tip model for a spherical tip, after the assumptions detailed in [112]. Figure reproduced from [110].

We have assumed here a perfectly flat sample, and following Tersoff and Hamann, we assumed only the s -wave tip state contributes to the measured signal. The reality is that

for typical tip materials such as tungsten or platinum/iridium, d -state orbitals contribute nearly all of the tip density of states at the Fermi level, and other types of states can contribute meaningfully to the signal[110]. The same is true on the sample side, where different surface electronic states imply a different atomic corrugation, further complicating efforts to determine an accurate value for the lateral resolution. While the true resolution of STM is difficult to determine, it has been shown experimentally to be much better than these earlier approximations[120, 121]. Ultimately, it is clear that to achieve reliable atomic resolution we must have sharp probes, eliminate disturbances such as surface contaminants which pollute the tunneling junction, and eliminate noise and vibration which render the tip-sample separation unstable.

2.2.2 Spectral Resolution

To determine the energy resolution during an STS measurement, or the spectral resolution, one must take into account more than just geometric factors. Anything which may change the measured density of states will affect the resolution. Thermal fluctuations due to temperature are always a factor, as are the fluctuations caused by the electronics (lock-in mechanism). We will assume the tip is held at a constant height during each measurement, else we would have to include terms due to the change in height, for example due to vibration of the tip with respect to the sample surface.

First, let us consider the fluctuations due to temperature. A more complete expression for the tunneling current is:

$$I(V) \cong \int_{-\text{inf}}^{\text{inf}} \rho_S(E) \rho_T(E - eV) M(E, V, z) \left(f(E - eV, T) - f(E, T) \right) dE \quad (2.13)$$

where ρ_S and ρ_T are the local density of states of the sample and tip, respectively, M is the tunneling matrix, and $f(E) = (e^{E/k_b T} + 1)^{-1}$ the Fermi-Dirac distribution. Following

the Bardeen approximation, where the sample and tip are considered as two parallel plates separated by a barrier, we can determine the current due to electrons tunneling from occupied states of the sample into unoccupied states of the tip through the Fermi Golden rule:

$$I_{S \Rightarrow T} = \frac{2\pi e}{\hbar} \sum_{u,v} f(E_u) (1 - f(E_v - eV_b)) |M_{uv}|^2 \delta(E_u - E_v + eV_b) \quad (2.14)$$

where the delta function ensures we have energetically aligned the sample and tip via the tunneling bias, V_b . Inserting now the density of states into the expression, we can write it as the integral:

$$I_{S \Rightarrow T} = A \int_{-\inf}^{\inf} \rho_S(E) f(E) \rho_T(E - eV_b) (1 - f(E - eV_b)) |M|^2 dE \quad (2.15)$$

where A collects the constants in the equation.

Likewise, we can write the contribution to the current due to electrons tunneling the other way, from occupied states of the tip into unoccupied states of the sample.

$$I_{T \Rightarrow S} = A \int_{-\inf}^{\inf} \rho_T(E - eV_b) f(E - eV_b) \rho_S(E) (1 - f(E)) |M|^2 dE \quad (2.16)$$

Then, the total current flowing between the tip and sample is given by the difference,

$$I = I_{S \Rightarrow T} - I_{T \Rightarrow S} = A |M|^2 \rho_T(0) \int_{-\inf}^{\inf} \rho_S(E) [f(E) - f(E - eV_b)] dE \quad (2.17)$$

$$\text{then, } I \propto \int_{-\inf}^{\inf} \rho_S(E) [f(E) - f(E - eV_b)] dE \quad (2.18)$$

$$\text{and } \frac{dI}{dV} \propto \int \rho_S(E) \left[-\frac{\delta}{\delta(eV_b)} f(E - eV_b) \right] dE \quad (2.19)$$

where as before, we treat the tip's density of states, ρ_T , as being constant across the energy range of interest. The term in square brackets is responsible for the thermal fluctuations, and

is approximately $3.5k_bT$. At room temperature, this accounts for about 80meV of broadening, and at $T = 10$ K, about 3 meV.

We can also determine the noise due to the experimental setup. In STS, we use a lock-in amplifier (LIA) to extract the dI/dV signal. The bias voltage has a small AC component added to the DC portion, such that $V_b = V_{DC} + V_{AC}\cos(2\pi\omega_0t)$, where ω_0 is the excitation frequency of the system. The current then becomes:

$$I(t) = I(V_{DC}) + g(V_{DC})V_{AC}\cos(2\pi\omega_0t) + \text{noise and higher order terms} \quad (2.20)$$

The signal is demodulated by the lock-in amplifier, but the oscillation contributes a term of approximately $2.5eV_{AC}$ to the noise. Typical values for V_{AC} are on the order of 1-10mV, thus this portion contributes anywhere in the range of 2.5-25 meV. The energy resolution is then determined by the squared sum of the thermal and LIA noise,

$$\Delta E = \sqrt{(3.5k_bT)^2 + (2.5eV_{AC})^2} \quad (2.21)$$

It is clear that for STS measurements, as we are free to choose the magnitude of the AC component, the spectral resolution is mainly limited by the temperature at which we conduct experiments. This detail is relevant in particular to samples such as those in Chapter 4, where the base temperature is limited by the need to achieve sufficient tunneling current on the semiconducting samples.

2.3 System Descriptions and Capabilities

Besides the experiments presented in the remaining chapters of this thesis, a considerable amount of time was spent installing, testing, and developing procedures for the STM and surrounding equipment in the lab. The remainder of this chapter will describe the instrumen-

tation of the main system used in these experiments, a commercial RHK PanScan Freedom STM, and the techniques which support its use. Where appropriate, standard operating procedures (SOPs) have been prepared to provide clear directions and to reduce the margin of error when performing more complicated or infrequent operations. Some examples of such SOPs are included in the appendices of this thesis.

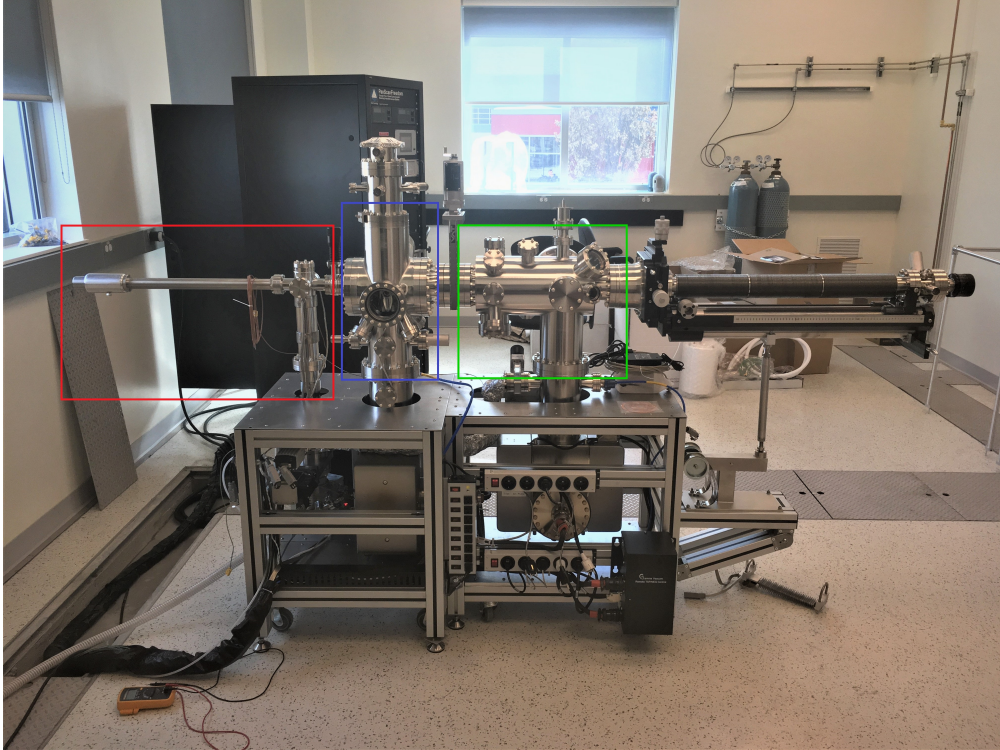


Figure 2.5: RHK PanScan Freedom STM. **Red:** Load-lock chamber and transfer arm. **Blue:** SPM Chamber. **Green:** Sample preparation chamber.

As was demonstrated in the derivation of lateral and spectral resolution, even a small change in the tip-sample distance can have large impacts on the exponentially decaying current. Therefore, to image samples with atomic resolution and to acquire reliable density of states measurements, a high degree of control is required on the tip-sample separation, the vibrational and electrical noise, and the sample and tip conditions [110, 115]. In order to satisfy these constraints, each part of the system surrounding the STM must be designed

to provide a controlled and stable environment.

First, we will describe the elements which enable us to perform tunneling experiments reliably. Most important to STM is the condition of the interface being measured. The sample must be isolated not only from external sources of noise, but also from sources of possible surface contamination. To that end, the STM is contained in an ultrahigh vacuum (UHV) system, meaning with pressures on the order of 10^{-10} Torr. To understand why this is needed, consider the time it takes a surface in air to be coated by the surrounding gas. Under ambient conditions (760 Torr), the mean free path of molecules is about 70 nm[122]. At this pressure, a surface will be covered by a monolayer in less than 1 ns. At the typical pressure of experiments (UHV: 10^{-10} Torr or less), this time is increased to 10^4 s. To study clean interfaces, it is thus clear that UHV is the appropriate environment. However, achieving UHV imposes design constraints on the STM not present for systems operated in air. The STM must be contained in a rigid, leak-tight environment (Figure 2.5). Outgassing becomes a serious issue, so the chamber is made of a low outgassing metal such as stainless steel. A periodic bakeout procedure is required to remove adsorbed molecules, especially water vapour, from the chamber's inner surface before it can achieve its ultimate base pressure. The exact bakeout procedure is presented in Appendix 8.7.

In our set-up, UHV is achieved via multiple stages of pumps, each operating in a different range of pressures. To maintain a clean environment and avoid excessive pump down times, the larger volumes of the SPM and preparation chambers are held at UHV continuously, and samples are introduced to the system through a "load-lock" chamber. Pumping down the entire volume of the system from atmospheric pressure can take days – the much smaller volume of the load-lock is pumped down to 10^{-8} Torr in about an hour, and its much smaller volume will barely affect the SPM chamber pressure when the gate valve which separates them is opened. To reduce the impact of this pressure difference, the load-lock is flushed with high

purity (99.9993%) nitrogen gas when opened to air. The positive pressure difference between the load-lock chamber and atmosphere limits the amount of gases which enter the system, replacing them instead with nitrogen gas which is readily pumped out. Once samples are exchanged and the load-lock is closed, two pumps work in tandem to bring it to high vacuum pressures. First, a dry roughing pump brings the load-lock from atmospheric pressures down to $\sim 10^{-4}$ Torr. A turbo molecular pump (TMP), which uses fast spinning blades to knock particles out to the roughing pump, can then bring the chamber to high vacuum ($\sim 10^{-8}$ Torr).

The main chambers of the system are kept under UHV through a combination of ion pumps and titanium sublimation pumps (TSP). Ion pumps use a cloud of electrons to ionize incoming gas molecules. A cathode generates an electric field which accelerates the ionized molecules towards the pumps and out of the main chamber of the system. TSPs are used to remove residual gases in the chamber. By passing a high current (10s of Amperes) through a titanium filament (*“flashing”* or *“burping”* the TSPs), the metal is brought to its sublimation temperature and the nearby chamber walls are coated with titanium. Residual gases which strike the walls have a high probability of sticking to the reactive metal coating, effectively removing them from the chamber. Eventually, the Ti coating will be dirty and a new layer can be deposited by flashing the TSPs again. In order to extend the active lifetime of the TSPs, three filaments are installed in each chamber, and their status is monitored on the pump control unit. Both ion pumps and TSPs require little to no maintenance, with the Ti filaments needing to be replaced only after several years of regular use.

An important feature of TSPs and ion pumps is the absence of moving parts which would introduce mechanical noise to the system. The exponential dependence of the tunneling current on distance makes even small sources of noise significant. The STM signal is monitored at all times by an oscilloscope, through which sources of noise can be identified. The

most obvious peaks that might be seen in the noise spectrum are those occurring at discrete frequencies, for example, noise from the building (5-10Hz), people walking across the floor (2Hz)[123], vehicles passing outside (5-25Hz)[124], or the power line frequency signal (60Hz and its harmonics). The STM's mechanical (turbo molecular and roughing) pumps are also significant sources of noise. The RHK STM uses a closed-cycle cryostat which brings many conveniences to the experiment, yet also introduces a more serious hurdle in the form of continuous vibrational noise in a part which must operate very close to the STM head. To mitigate this issue the cryostat is suspended above the STM chamber on a supporting structure, and is set exactly such that the cold finger which inserts into the SPM chamber is decoupled from the system walls to avoid transmitting any vibrations. Beyond this, several stages of passive vibration isolation are used to combat vibrations in general: the roughing pumps and the cryogenic condenser unit are isolated from the STM on a separate floor, and the instrument sits on a rigid table in a room which itself is separated from the building on a concrete slab. The STM head is mechanically rigid and is suspended by a spring suspension stage, part of which can be seen in Figure 2.6b. The load-lock's TMP is shut off during normal operation of the STM, and any procedure which involves touching the SPM chambers is avoided during scanning.

Electronic noise can be more subtle, including Johnson noise from the preamplifier feedback resistors (above 100kHz), the $1/f$ noise from the tunnel current power spectrum (10Hz to 100kHz), and power line frequency (60Hz and its harmonics)[115, 125]. The STM's electronics must meet the required precision to measure and control the tiny fluctuations in current and voltage from the signal, while also minimizing electrical noise. During scanning, the tip-sample separation will be on the order of 1 nm or less, and must be controlled with an accuracy of better than 1% of this value to produce meaningful results[115]. Pre-amplifiers help to overcome background electrical noise for the exceedingly small tunneling signal, which

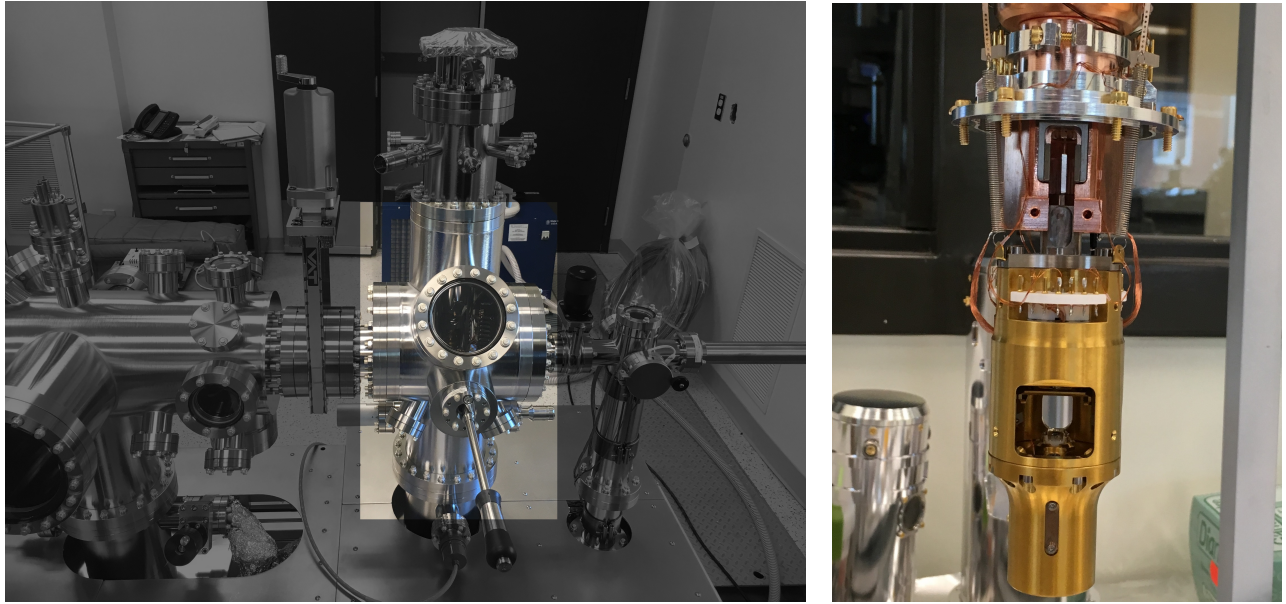


Figure 2.6: (a) STM chamber (highlighted area). (b) STM head, removed from the UHV chamber.

is on the order of picoamperes. The exponential signal then passes through a log amplifier to convert it to a linear signal. The electronics of the STM circuit must minimize capacitance and are ideally placed at the minimal distance possible from the tunneling junction to avoid electrostatic coupling and interference.

Beyond these sources of mechanical and electronic noise, there is also variation in the tip-sample interaction due to thermal noise. Of course, low temperature capability offers the opportunity to study physics which only occur at extreme temperatures. An example in this thesis will come in Chapter 6, where the antiferromagnetic transition temperature of MnBi_2Te_4 is 25K[126]. But more so, lower temperatures offer several improvements to the performance of the system. First, decreasing the temperature of the inner chamber can have a cryo-pumping effect, adsorbing gases from the system onto the walls in a manner similar to the function of the TSPs. Another issue mitigated by lower temperatures is thermal drift – dynamically varying fluctuations which limit the maximum achievable resolution. As was

demonstrated in Section 2.2.2, spectroscopy is negatively impacted by temperature, which not only determines the energy resolution of the measurement, but also the accuracy of the tip’s positioning, i.e., how well the tip can be kept at a specific point over an extended period of time.

In the RHK STM used in this thesis, low temperature is maintained by the closed-cycle cryostat, which continuously recycles evaporated helium gas into liquid and transports it to a cold finger near the STM head. A vapour barrier between the end of this cold finger and the top of the STM head is used to transfer heat from the STM into the He gas, which is recaptured and condensed to a liquid again. The closed-cycle cryostat invokes a small penalty on the base temperature of the system, reaching sample temperatures of 9K instead of the 4.5K achievable from bath cryostats. Other low-temperature systems might consist of a bath of cryogenic liquid in contact with the STM chamber, acting as a heat sink which cools the system – and which either waste or recycle the evaporated He gas. In fact, the closed-cycle system is analogous to a miniature helium recovery system which is continuously “refilling” the STM’s cryostat. It also removes the need for He refill cycles which frequently interrupt experiments and demand large quantities of liquid helium, instead starting from inexpensive gaseous helium. Best practices for operation of the closed-cycle cryostat are described in Appendix 8.6.

For instances where a sample may be insufficiently conductive at the base temperature of 9K, the STM has variable temperature control, allowing stable operation at any temperature from RT (300K) down to LT (9K). The primary use of this feature is to eliminate drift to the extent possible, which improves the resolution and stability of experiments. Some examples of this use case are found in Chapter 4, where spectroscopy on semiconducting 2D materials was obtained at temperatures ranging from 75-300K. Measurements at intermediate temperatures require separate piezo calibrations (see Appendix 8.4), and additional efforts

must be placed to ensure temperature stability during the experiment. Not just the sample, but also the nearby components of the STM head must be allowed to thermalize to the desired temperature, otherwise there will be excessive drift as the temperature changes. This process takes a few hours, and care must be taken to avoid contaminating the sample during large increases in temperature, as cryo-regeneration occurs (the inverse of cryo-pumping, wherein trapped gases are now released from the walls of the chamber and could deposit on the sample surface).

Coarse positioners are used to move the tip to different areas on the sample and to retract the tip. In practice, these move the sample plate relative to the tip, and sacrifice precision for larger range. During scanning, positioning is achieved through piezoelectric actuators (“piezos”). To image individual atoms, the tip must be able to move on this length scale accurately - piezos can achieve this resolution. Fine positioning of the tip is controlled by a 4-quadrant piezo scan tube which controls the lateral motion (X+, X-, Y+ and Y- quadrants), and another piezo which controls the Z motion. The range of the piezos is 10 μ m at room temperature, and at low temperature this value is reduced by an order of magnitude. While most of the electronics are limited to an operating range of $\pm 10V$, the operating range of piezos is on the order of $\pm 150V$. To fully extend the piezos, it is therefore necessary to include a high voltage amplifier[115].

Piezoes suffer from a few problems, namely hysteresis and creep. The response of piezos to applied voltage is nonlinear, but the fields applied are so small that this effect is minimal[115], at least on the scanning range used to image atoms. When imaging large features (near the maximum range of the piezo), higher fields must be applied and these nonlinear effects become important again. Nonlinearities and creep can have similar effects on imaging as thermal drift, but these can be eliminated by controlling the position through charge control amplifiers (a capacitor in series with the piezo circuit).

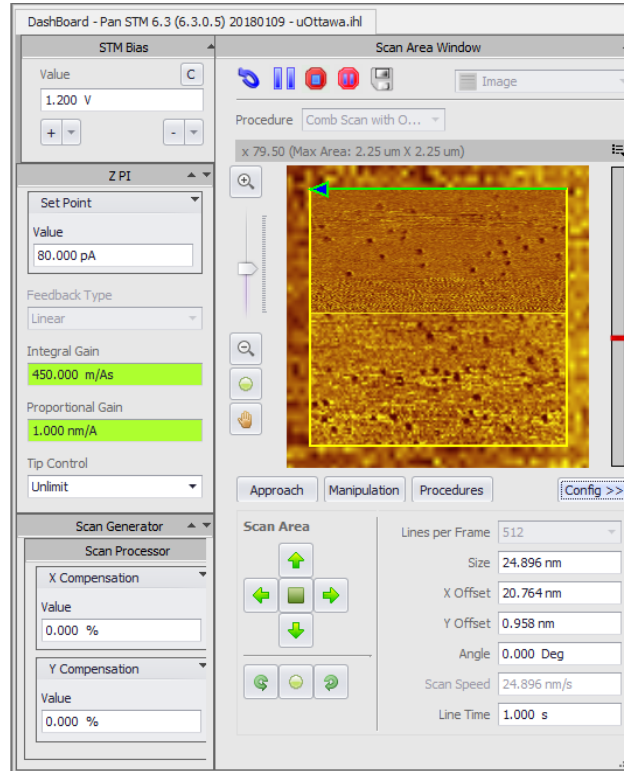


Figure 2.7: RHK STM User Interface. All of the parameters, including bias voltage, tunneling current, gain, scanning speed, and tip position are controlled through the software. The “Scan Area Window” shows data as it is being acquired.

A feedback loop[115] is used to control the tip-sample distance[115]. For a fixed bias voltage and reference tunneling current chosen by the operator, the feedback loop reacts to the changing gap conditions to maintain a constant current by adjusting the tip-sample distance. This is used initially to bring the tip into tunneling range, and during scanning the feedback loop reacts to the changing topography by adjusting the height of the tip. The feedback mechanism determines the ultimate scanning speed the system can reach – microsecond[127] response times can be achieved, but typical setups will have millisecond responses[115]. This is achieved through a combination of integral and proportional gains, which can be adjusted between scans (Figure 2.7). For spectroscopy, a lock-in amplifier is used to directly measure the dI/dV signal, as opposed to relying on the noisier numerical derivative.

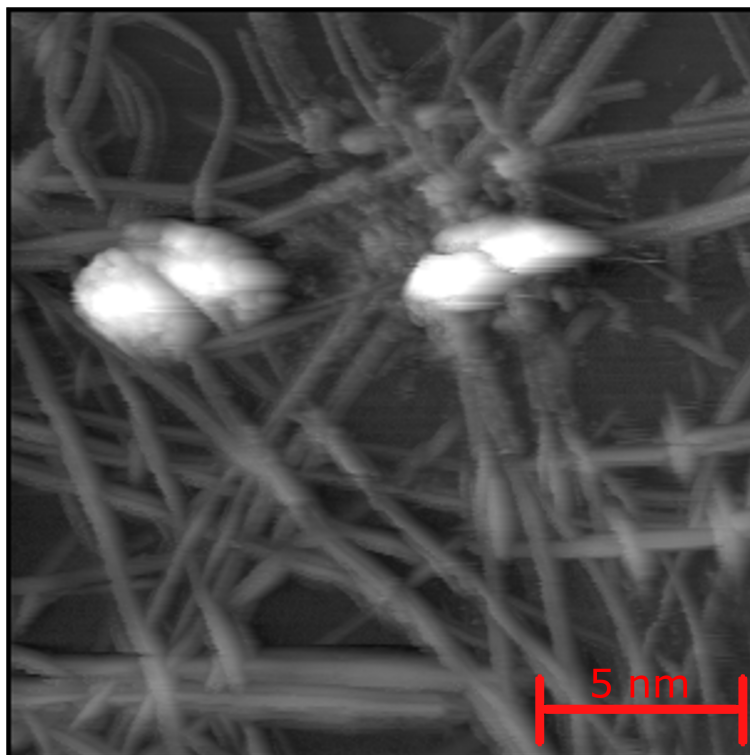


Figure 2.8: Image of carbon nanotubes from a double tip on a sample we analyzed – each nanotube is visible twice in the image, as a result of tunneling through multiple tips.

All of the above are essential to acquiring data, but the quality of the tip and sample is paramount for obtaining results that are of high quality. Tips must be metallic, with a flat density of states across the energy region of interest. They must have a singular apex, else a “double-tip” effect occurs if there is simultaneous tunneling through multiple separate “tips” (Figure 2.8). The processes used to make atomically sharp probes are described in Appendix 8.2. During scanning, the short distance from probe to surface means the tip can easily pick up adsorbed molecules. If the tip or surface is covered in contaminants (e.g.: oxides, polymers) the tunneling barrier is effectively increased and image quality is reduced, limiting the resolution. Thus, great care is required in preparing samples – in order to ensure the highest chance of success in subsequent experiments, they must be “atomically clean”. For simple bulk crystals like those used in Chapters 4 and 6, the surface is cleaved following the procedure described in Appendix 8.3.1. With this method, the newly cleaved surface

is exposed for only a short period of time before being introduced to UHV, and this time is spent in an inert environment which prevents water and hydrocarbons in the air from depositing on the surface.

Chapter 3

Fabrication of Atomically Clean van der Waals Heterostructures

Fabrication of van der Waals heterostructures for STM experiments requires that not just the interfaces, but most importantly the final exposed surface be free of contaminants. Transfer procedures for van der Waals devices typically involve a dry transfer using polymers whose adhesive properties can be tuned, for example via temperature, to selectively pick up or drop off flakes. Such polymers are not always easy to clean from TMD surfaces, requiring high temperature annealing or aggressive chemical etching which can affect the device properties. In addition, it can be challenging to pick up monolayer flakes with polymers which are otherwise ideal for dry transfers of thicker flakes. An example of a van der Waals heterostructure assembled using the PVA/PMMA method (PVA: polyvinyl acetate; PMMA: poly(methyl methacrylate)) is presented in Figure 3.1. Electron beam lithography was used to pattern contacts (5 nm Ti / 120 nm Au) to the sample on the insulating Si/SiO₂ substrate. After a standard chemical wash (acetone, isopropanol, dried with N₂), and despite an extensive annealing time (15 hours @ 300°C in 60 sccm of H₂/Ar, and 16 hours at 340°C in vacuum (10⁻⁸ Torr)), the surface remained contaminated with enough polymer to impede STM imaging. Clearly, a technique which avoids bringing the final surface into contact with polymers, while also permitting the transfer of any arbitrary 2D material, is highly desirable.

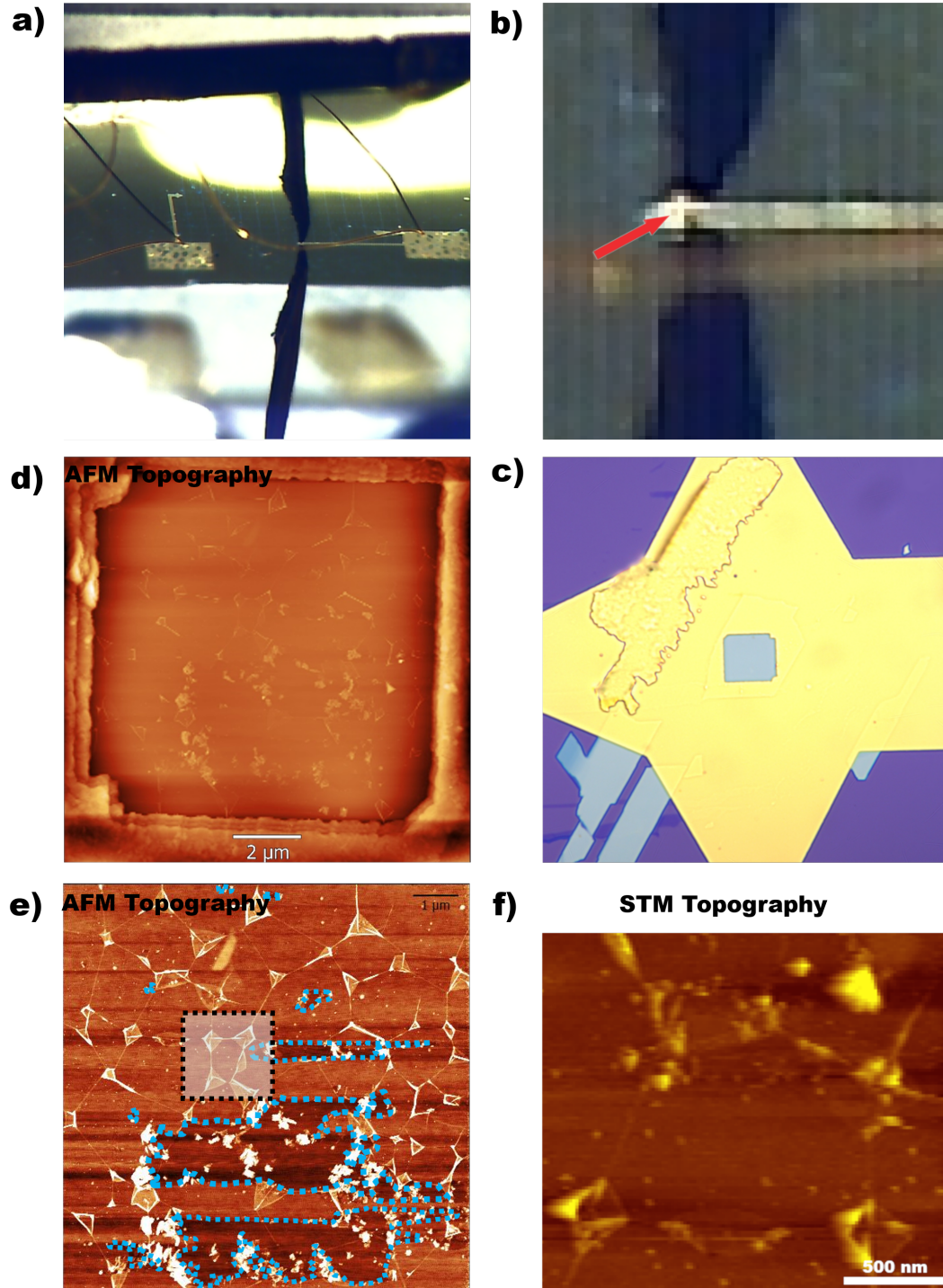


Figure 3.1: A monolayer graphene on bulk ReS₂ sample assembled with the PVA/PMMA method. (a) Optical image of the sample inside the STM system. The probe and its reflection are seen approached to the sample. (b) Optical image of the STM tip approached to the sample, with the camera fully zoomed-in. The sample can be seen as a single pixel of a different colour from the gold contacts. (c) Optical microscope image of the sample and metal contacts. (d,e) AFM topography of the sample. Blue dotted lines indicate regions where the graphene layer is “torn”, revealing the bulk ReS₂ underneath. (f) STM topography ($V_B = 1\text{V}$, $I_T = 50\text{pA}$) of the white boxed area in (e).

To address these challenges, a fabrication method which was named the “inverted” dry transfer technique was developed to create atomically clean van der Waals heterostructures suitable for use as STM devices, following [2]. This process is similar to the now-common dry-transfer techniques for fabrication of van der Waals devices, with two notable differences. In dry transfer techniques, it is common to use bulk flakes of the insulating 2D material hexagonal boron nitride (hBN) as the last (top-most) component of the device. This is due in part to its use as a convenient dielectric material for gating purposes, but also as an encapsulating material which protects the device from environmental contamination and degradation, improving device performance[128]. For STM samples however, the hBN encapsulating layer is an insulator which restricts access to the surface and thus cannot be used.

The order in which each constituent layer in a device is picked up and the technique by which they are transferred to the final substrate can vary based on the application. The simplest and most common method is to pick up a singular flake, and drop it off from the polymer at a target location. This process can be repeated to assemble heterostructures with successive transfers, one layer at a time. However, the layers will come in direct contact with the polymers used in the transfer procedure, which would introduce contamination to the surface and interfaces of the device. To avoid this issue we introduce another modification to our procedure. Here, the device is assembled entirely on a singular polymer stamp through a series of pick-up steps. The flakes are picked up in the opposite order that they will take in the completed device (i.e., bottom-up, beginning with the flake which will sit on the substrate). The entire stamp with the device is then removed from its supporting glass slide, flipped, and placed directly on the final substrate, such that the heterostructure sits above a layer of polymer on the substrate. In this way, neither the interfaces between layers nor the surface of the device makes contact with polymers – only the bottom-most surface of the device, which was already inaccessible to the STM, does so. The procedure is described in detail below.

3.0.1 Inverted van der Waals heterostructure fabrication

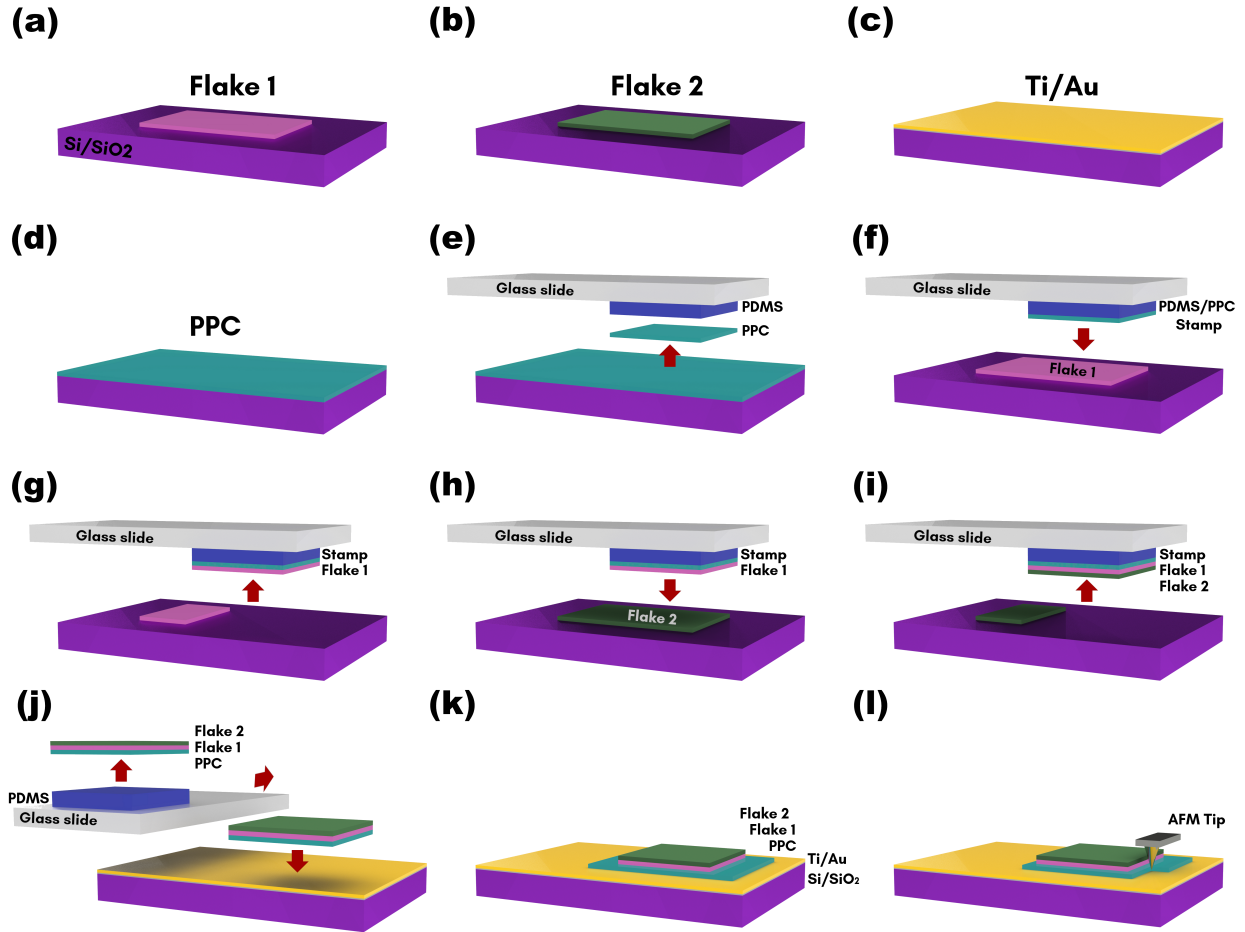


Figure 3.2: Inverted transfer procedure, step-by-step. (a) Flake 1 (pink), which will become the bottom-most layer of the heterostructure, and (b) Flake 2 (green), the top-most layer, are prepared on Si/SiO₂ substrates by mechanical exfoliation. (c) A Si/SiO₂ substrate is patterned with 5nm Ti/50nm Au by e-beam metal deposition. (d) A layer of PPC is spin-coated onto a sacrificial substrate. (e) The PPC is transferred onto a PDMS stamp on a glass slide. (f) The PPC-PDMS stamp is pressed onto Flake 1. (g) With heat applied to the bottom substrate, the adhesion of the PPC to the flake allows the section touching the PPC to be picked up. (h, i) The press and pick up steps are repeated on Flake 2. j) The stamp is separated by detaching the PPC and heterostructure from the PDMS, and the glass slide with the PDMS is discarded. The PPC-heterostructure stack is then placed onto the target substrate. k) The structure, now substrate-contact-PPC-flake 1-flake 2, has been inverted such that the last flake to be picked up has become the top surface. l) A combination of annealing and AFM brooming steps are used to clean the remaining PPC from the areas surrounding the sample.

The inverted transfer procedure begins by preparing a polymer stamp, similar to those used in the typical dry transfer techniques. Polydimethylsiloxane (PDMS, or gel-pak, thickness = 0.432 mm) is cut into a 1.5 mm x 1.5 mm square and placed on a glass slide. A second polymer, polypropylene carbonate (PPC, 15% dissolved in anisole) is spin-coated onto a substrate (3000 rpm for 1 minute; cured at 75° C for 5 minutes), then a tape-frame is placed around the edges of the substrate to lift the PPC off. The PDMS stamp on the glass slide is treated via oxygen plasma (50W and 53.3Pa for 2 minutes) to roughen its surface, then the PPC is placed onto the PDMS immediately after the etch is completed. This structure of PPC-PDMS-glass slide forms the “stamp” which can be used to pick and place flakes. The PDMS square serves to push the PPC out from the glass slide, ensuring a small first point of contact at a targeted location on the substrate. An added benefit of this stamp is also to press out air bubbles which normally appear during transfer procedures, laminating the surface smoothly and increasing control during the stacking process, as compared to older procedures (see [129] for details).

Mechanical exfoliation is used to isolate monolayer or bulk flakes from bulk crystals onto Si/SiO₂ substrates. Once suitable flakes are identified, the optical microscope transfer setup described in [129] is used to assemble the heterostructures. Flakes are aligned and assembled in sequential pick up steps on the same stamp, beginning with the flake which will be the bottom-most crystal of the completed device (*flake 1*), followed by the next flake (*flake 2*), and so on. For the entire transfer process, the stage is held at 40°C by the built-in resistive heater, where the polymer’s adhesion to the flakes is greatest. After all the layers have been picked up, the PPC is separated from the PDMS using the tape frame, and placed onto a gold-coated or pre-patterned substrate (5nm Ti/50nm Au, prepared by electron beam metal deposition). From the bottom up, we now have a structure consisting of *substrate—contact—PPC—flake 1—flake 2*. Note that the last flake to be picked up has now

become the top-most flake of the device (i.e., the device has been inverted) and that at no point during the transfer procedure did the interfaces or the surface of the heterostructure come into contact with any polymers.

The next step is to remove as much of the PPC layer as possible. Next, the substrate is placed on a hotplate (160°C for 5 seconds). This heating step solidifies the polymer and firmly sticks the sample in place. If observed in a stereo-microscope during this heating, a change in colour can be seen sweeping across the surface, which indicates the evaporation of the anisole from the PPC. For samples which should not be exposed to high temperatures in air, this heating step on the hotplate can be skipped, however, this carries the risk of the sample being removed with the polymer when it is cleaned in the following annealing step. In principle, this step could be performed in an inert environment such as a glovebox or vacuum furnace, however, this was not required for the materials used in this thesis. Using a needle to poke at the polymer, a square of a few hundred microns or smaller is cut around the device. The majority of the polymer can then be separated and removed from the substrate. It is important to make smooth cuts along the edges, else they could roll up or fold over the sample during any of the following heating steps.

To remove the remaining polymer, the sample is then annealed (10 hours at 300°C) in forming gas (60sccm H₂/Ar). This step not only cleans the substrate, but also guarantees the bottom-most flake of the heterostructure makes good electrical contact to the gold contact below. Now, one can optionally use electron beam lithography to pattern contacts onto the heterostructure. If for example one of the layers is an insulator (e.g. hBN) and is not completely covered by the flakes above it, metal contacts can be deposited above to protect from accidentally approaching the tip on the insulator and crashing it. Afterwards, the sample is annealed in vacuum (30 minutes at 300°C) in a homemade vacuum furnace (Appendix 8.8) to ensure the surface of the device is clean and to further remove the residual

PPC or any e-beam resists from the substrate. Finally, we employ AFM “brooming” to guarantee the sample and surrounding areas are clean [55, 130], the procedure for which Justin Chouinard developed and described in [131]. This is an important step as, especially for smaller samples or those on unpatterned gold-coated substrates, it is possible that the first approach with the STM tip will be only near the sample, not directly on it. To protect the tip from contamination, which exists only on the substrate, AFM brooming is used to push polymer further away from the areas surrounding the sample. At the same time, detailed AFM topography of the sample is taken to map out the surface.

The substrate is mounted to a standard Omicron-style stainless steel STM plate using conductive silver epoxy (Epo-tek H21D). The epoxy also provides good electrical contact to the sample, by ensuring the sample plate is connected to the gold on the substrate. For patterned substrates, samples are connected via wire bonding with gold wire.

Results from samples successfully fabricated following the completed procedure are presented in Chapter 5.

Chapter 4

Defects in bulk semiconducting TMDs

Intrinsic defects, such as grain boundaries, vacancies, adatoms, and substitutional impurities are ubiquitously present in graphene and transition metal dichalcogenides [60, 132–134]. Harnessing the properties of TMDs for atomic scale optoelectronic devices requires a detailed understanding of the nature and effects of structural lattice defects on the material properties. Defects can influence the performance of devices through the formation of electronic states within the semiconducting gap [135, 136], can modify the excitonic transitions and photoluminescence response [137], can behave as atom-like quantum emitters [138, 139], and can affect the catalytic properties[140]. Although imaging techniques can visualize surface defects of bulk TMDs[31, 141, 142], identifying their nature and correlating their presence with properties of the material remains challenging. For example, one of the most common imaging techniques, electron microscopy, can result in knock-on sputtering of chalcogen atoms[31], making it impossible to distinguish the intrinsic defects. Moreover, in the case of some TMDs like ReS₂, the larger atomic number of the metal atoms can prevent identification of the nature of defects. Therefore, less invasive techniques like scanning tunneling microscopy and spectroscopy (STM/STS) can be invaluable in imaging and determining the properties of lattice defects.

Parts of this chapter follow closely or partly reproduce text from the published paper, “Ryan Plumadore, Mehmet Baskurt, Justin Boddison-Chouinard, Gregory Lopinski,

Mohsen Modarresi, Pawel Potasz, Pawel Hawrylak, Hasan Sahin, Francois M. Peeters, and Adina Luican-Mayer, *Prevalence of oxygen defects in an in-plane anisotropic transition metal dichalcogenide*. (2020) Phys. Rev. B. 102, 205408”. The Declaration of Authorship at the beginning of this thesis (*pages iii-iv*) lists the contributions of each author to this work in detail.

This chapter presents results of scanning tunneling microscopy and spectroscopy characterization of defects on two bulk, semiconducting 2D crystals, WSe₂ and ReS₂. In both cases, bulk crystals were prepared by first adhering them to standard stainless steel STM sample plates with conductive epoxy (Epo-tek H21D). The surface was prepared using the quasi-in situ cleaving technique described in Appendix 8.3.1 to ensure minimal exposure to air before experiments. Scanning was performed under UHV environment, with data collected at temperatures between 75-300K.

For the first of these, WSe₂ (HQgraphene), the goal of the experiments was to determine the defect density on a typical device-sized area (100 nm²) on commercial crystals. While performing these measurements, the band structure of the crystal and the influence of defects on the local density of states were measured by scanning tunneling spectroscopy. Atomic resolution images of defects provide further insight into the possible nature of the defects in WSe₂.

The next TMD to be examined was ReS₂ (HQgraphene), where the structural and electronic properties are determined through a combination of STM/S and *ab initio* calculations. In this case, the goal was to fully characterize the defects, expanding upon previous work from my MSc thesis[1]. Spectroscopy and atomically resolved topography on defects was measured, supported by simulated STS and density of states calculations, and by X-ray Photoelectron Spectroscopy (XPS) characterization of the crystals to determine elemental concentrations. The experimental and theoretical results indicated that the most common

defects in ReS_2 are oxygen atoms adsorbed at lattice-point defect sites.

4.1 Tungsten Diselenide (WSe_2)

The bulk WSe_2 crystals used for the experiments in this chapter are sourced from HQ-Graphene, and are the same used in other experiments within Prof. Luican-Mayer's group[143–145]. WSe_2 is a layered semiconductor in the $2H$ phase, with a hexagonal lattice wherein tungsten atoms are bonded to six equivalent neighbouring selenium atoms, with lattice spacing of $a = 3.28\text{\AA}$ [146–148]. Bulk WSe_2 has an indirect band gap of 1.2-1.3 eV, which becomes direct in the monolayer limit and increases to 1.6-1.7 eV. [149–155] As with any semiconductor, defects play an important role in tailoring its optical and transport properties. Defect states in TMDs could be used to manipulate the spin-valley degrees of freedom through defect-bound localized excitons[156–159]. TMDs usually contain a high density of chalcogen vacancies, and these can be passivated by oxygen[141], which in WSe_2 was shown to massively enhance the electrical- and photo-conductivity of monolayers[160].

In order to better understand the performance across samples incorporating semiconducting TMDs, it is important to determine the defect density, a number which can act as a tuning knob on the device properties. While a direct characterization of the types and functionalities of the defects present on the WSe_2 surface was outside the scope of this experiment, measuring the defect density can help explain differences in performance against heterostructures made from other 2D TMDs. For example, the defect densities reported on MoS_2 are in the range of $8 \times 10^{12} \text{ cm}^{-2}$ [161] to $2 \times 10^{13} \text{ cm}^{-2}$ [162] for crystals grown by chemical vapour deposition, and $5 \times 10^{12} \text{ cm}^{-2}$ [163] to $5 \times 10^{13} \text{ cm}^{-2}$ [164] for natural crystals. By comparison, defect densities in grown WSe_2 crystals range from $7 \times 10^{10} \text{ cm}^{-2}$ [165] to $2 \times 10^{11} \text{ cm}^{-2}$ [166], while the reported defect density on natural WSe_2 crystals is $1.1 \times 10^{12} \text{ cm}^{-2}$ [167]. Evidently, there is a variance in the defect densities for crystals obtained from

different methods or sources, and thus the goal of these experiments was to directly measure this quantity in our own WSe_2 crystals.

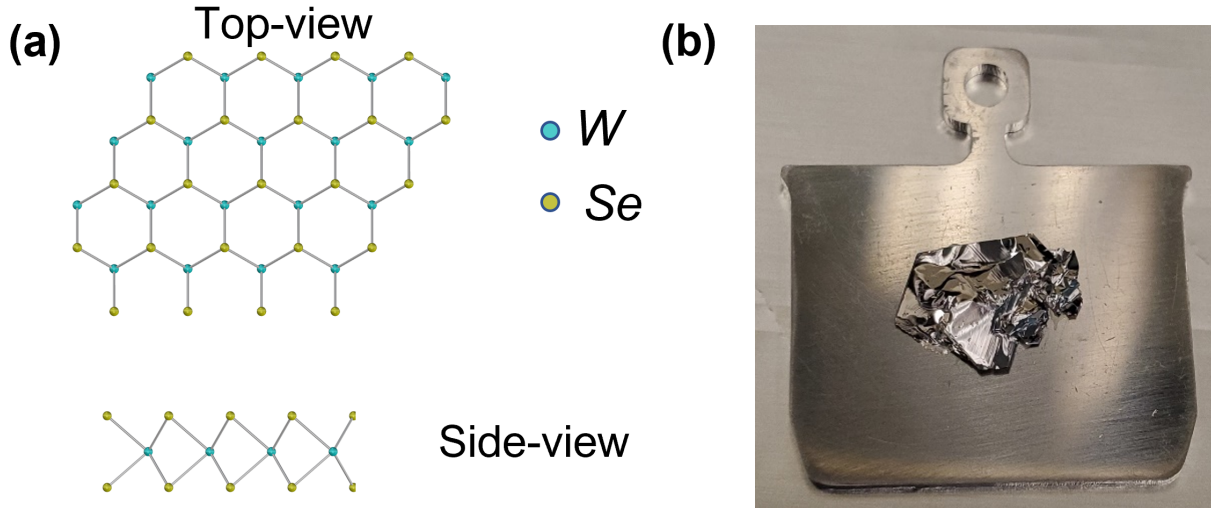


Figure 4.1: (a) Top and side view of the WSe_2 crystal structure. (b) Image of the WSe_2 crystal affixed to an STM sample plate.

To determine the number of defects on the surface, and to understand more about their effect on the band structure of the material, scanning tunneling microscopy and spectroscopy experiments were carried out. Bulk crystals from the same mother crystal as those used in [143–145] were affixed to stainless steel sample plates with conductive silver epoxy (Epo-tek H21D), and exfoliated in the load-lock under high purity N_2 flow as described in Appendix 8.3.1. The samples were not sufficiently conductive below 75K to achieve tunneling conditions, so, utilizing the heated STM stage and closed-cycle cryostat, measurements were performed at 300K, 90K, and 75K, using mechanically cut Pt/Ir tips, and were repeated with multiple tips across multiple separate areas across the bulk crystals.

4.1.1 Quantifying the defect density in WSe_2

The primary objective was to measure the defect density. Topographic images such as those presented in Figure 4.2(a) were measured at separate areas across the crystal surface. Point

defects in the surface appear as bright points surrounded by a dark halo (Figure 4.2(b)), or as dark spots (Figure 4.2(c)), as observed in STM reports on other 2D materials [141, 161, 163, 164, 168, 169]. Since the electrostatic influence of defects buried in deeper layers is diminished at the surface, the defects with the greatest contrast will be those in the top layer of the bulk crystal, and those with less contrast can be assumed to be in deeper layers. When determining the defect density only the top-most defects are considered, meaning those with the greatest contrast in a given image – shallow defects such as those in Figure 4.2(a) or Figure 4.3(b) are defects from layers beneath the surface. Such defects were not included in the overall tally, as the goal was to determine the defect density in a single layer of WSe_2 .

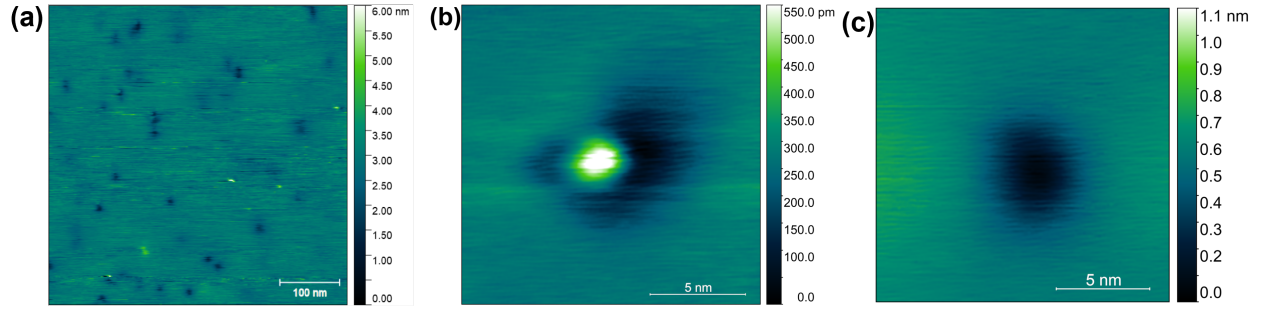


Figure 4.2: (a) Representative STM image ($V_B = -1$ V, $I_T = 250$ pA) of the WSe_2 surface with defects visible as dark or bright protrusions, and with subsurface defects appearing as faint dark spots. (b) Bright defect with dark halo ($V_B = -1$ V, $I_T = 200$ pA), and (c) Dark defect ($V_B = -1$ V, $I_T = 200$ pA).

The measured defect density across the WSe_2 surface was $1 \times 10^{10} \text{ cm}^{-2}$, or about one defect of any type inside the area of a typical $\sim 100 \text{ nm}^2$ device. Notably, this is around two orders of magnitude less than other reports in literature on WSe_2 crystals [167].

4.1.2 Further characterization of WSe₂ defects

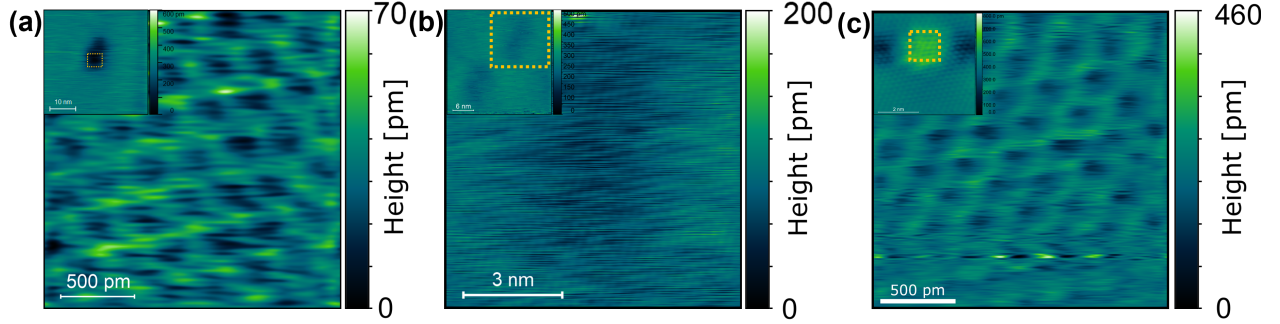


Figure 4.3: STM topography ($V_B = -1$ V, $I_T = 200$ pA) with atomic resolution on an assortment of defects in WSe₂: (a) dark, (b) subsurface, and (c) bright with dark halo.

While fully characterizing the nature of the defects was outside of the scope of this project, some effort was made to obtain atomic resolution images across the defects (Figure 4.3). The diameter of the defects extends across several unit cells, and the atomic registry is intact across the area of the defect. Since the STM contrast is a measurement of the local electrostatics at the surface, the apparent height of the defects does not necessarily represent their true height. A common observation in the literature is that the defects in TMDs are substitutional oxygen vacancies[141], though more measurements would be needed to confirm that suggestion in this case – for example, simultaneous non-contact AFM measurements or characterization with XPS or transmission electron microscopy (TEM) to search for elemental signatures would have aided in confirming the origins of the defects. Despite this, a feature which could be used to refute the presence of substitutional oxygen at vacancy sites is the presence or absence of in-gap states (IGS) within the band gap.

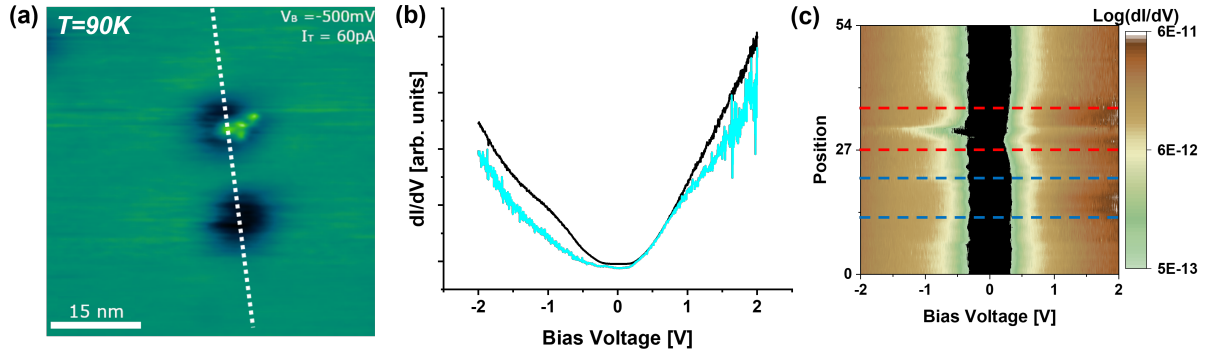


Figure 4.4: (a) STM topography ($V_B = -0.5$ V, $I_T = 60$ pA, $T=90$ K) of WSe₂ defects. (b) Average of all spectra measured across the undisturbed WSe₂ surface along the white dashed line (black) from (a), and average of spectra measured only on defects (blue). (c) Map of the individual curves along the STS line, with the positions of the defects marked by red (bright defect) and blue (dark defect) dotted regions.

As has been described previously by S. Barja *et al*[141], vacancy sites in TMDs are expected to host defect states within the band gap, and substitutional oxygen at such vacancy sites should suppress the IGS. To search for signs of IGS, scanning tunneling spectroscopy at intermediate temperatures (75-90K) was measured by taking line spectroscopy across defect sites. In this study, no IGS were observed from spectroscopy taken on defects. When comparing the average of spectra measured on defects sites against the average of spectra measured away from defect sites, a change in the structure of the valence band was observed. Notably, on a defect in Figure 4.4, the valence band maximum shifts down in energy by ~ 100 meV (Figure 4.4(b)), increasing the size of the band gap measured above the feature. Across the dark defect, which were the most commonly observed on the WSe₂ surface, the spectra are nearly undisturbed, showing neither IGS nor any significant modifications of the valence or conduction bands. Though certainly, the absence of the observation is IGS is not definitive, and more data would be required to prove this conclusion, altogether these results support the notion that the most common defects in WSe₂ are likely to be oxygen adsorbed on chalcogen vacancy sites, as has been reported in other 2D materials. Ultimately,

the measurement of the defect density at the surface in WSe_2 is particularly relevant to understanding the quality of this material as a component of heterostructure devices.

4.2 Rhenium Disulfide (ReS_2)

While most van der Waals (vdW) layered materials are isotropic within the plane, a number of them have lower in-plane crystal symmetry[170]. In-plane anisotropy in layered vdW materials gives additional functionality that has only just begun to be explored in black phosphorus (BP)[171], transition metal trichalcogenides (TiS_3)[172], rhenium disulfide (ReS_2), and rhenium diselenide (ReSe_2)[173]. Among them, ReS_2 attracted attention as a material that is stable under ambient conditions, with structural anisotropy that translates into further tunability in its electronic[174, 175], optical[176–180], and mechanical[181] properties. It was shown to be a tunable diamagnetic semiconductor[170, 182], and a candidate for energy storage[183] and memristive devices[184].

4.2.1 ReS_2 lattice and band structure

ReS_2 material is a group VII TMD which, when compared to a group VI TMD such as WSe_2 , has an additional electron on each metal atom. Structurally, ReS_2 is a distorted $1T$ structure which belongs to the $P\bar{1}$ space group[185, 186]. The additional electron in the d orbital of the rhenium atoms favors the existence of metallic Re–Re bonds, responsible for the formation of a superlattice of chains with diamond clusters of four Re atoms, as shown schematically in Figure 4.5(b). This structure was previously visualized by x-ray spectroscopy[185, 187] and electron microscopy [31]. Early scanning probe microscopy studies also provided indications of a Re chain structure[188–190]. When cleaved, the crystal orientation of the ReS_2 flakes is apparent, as they maintain the edges parallel to the rhenium chains. This feature is useful for identifying the orientation of a crystal for example in device fabrication[191, 192]. Indeed, in the large area STM topographic images, as presented in Figure 4.5(c), it was found that

terraces on the surface of ReS_2 follow the crystallographic directions with an angle $\gamma \approx 120^\circ$ between the a and b directions. The terraces and steps in Figure 4.5(c) correspond to single or double atomic layers, with their height measured as shown in the inset.

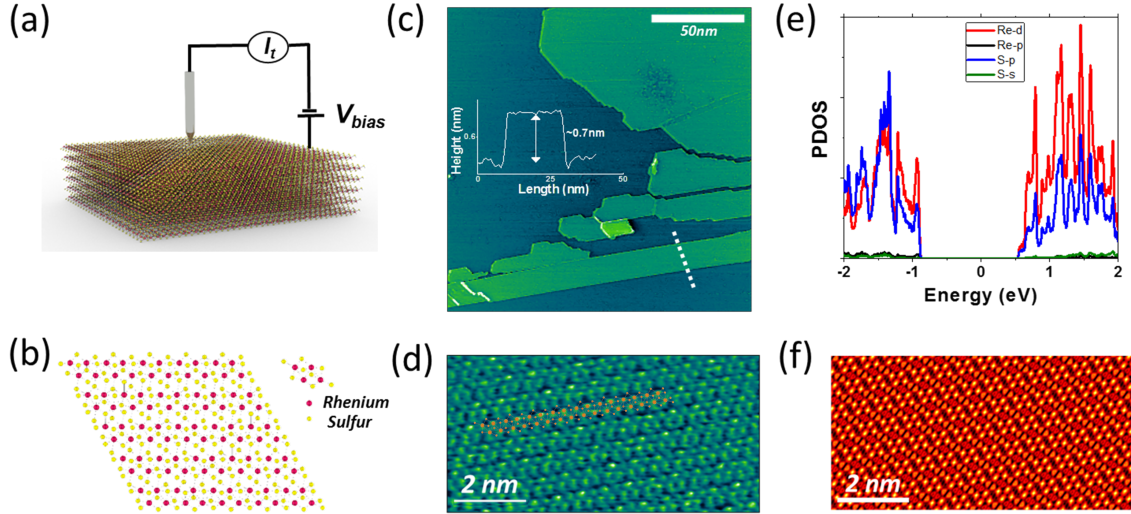


Figure 4.5: (a) Schematic of the STM experiment. (b) Top and side view of the ReS_2 structure. (c) STM topographic map of step edges on the surface of a ReS_2 crystal ($V_B = -1.60$ V; $I_T = 450$ pA). Inset: Height profile along the white dotted line. (d) STM topographic image highlighting the Re chains with a spheres model as a guide to the eye. (e) Calculated PDOS of monolayer ReS_2 . (f) Simulated STM image of the ReS_2 lattice.

In higher resolution images, presented in Figure 4.5(d), we observe the characteristic anisotropic lattice structure with elongated chains. One might be tempted to attribute the measured features to the topmost layer of sulfur (S) atoms[188] which is closest to the tip. However, a more accurate interpretation should consider that the contrast in the atomically resolved STM topographic images originates from local density of states (LDOS). Therefore, the complex dependence of the partial density of states (PDOS) at the surface layer on the energy at which the tunneling process occurs must be considered. The calculated PDOS using ab initio theory (performed by collaborators: Mohsen Modarresi (M.M.), Pawel Potasz (P.P.), and Pawel Hawrylak (P.H.)) is shown in Figure 4.5(e). The density of states is dominated

by the rhenium d -orbitals, which is related to the flat band dispersion around the top of the valence band (VB) at the Γ point. At higher energies, band crossings lead to a substructure in the density of states. It was found that, within the energy range of this experiment, the rhenium d -orbitals (in red in Figure 4.5(e)) are responsible for the largest contribution to the density of states. This implies that the metal atoms are predominantly involved in the tunneling process and therefore provide the contrast in the atomically resolved topographic images. This is further confirmed by simulated images of the STM measurement (performed by collaborators: Hasan Sahin (H.S.), and Francois M. Peeters (F.M.P.)), shown in Figure 4.5(f), the details of which can be found in [3].

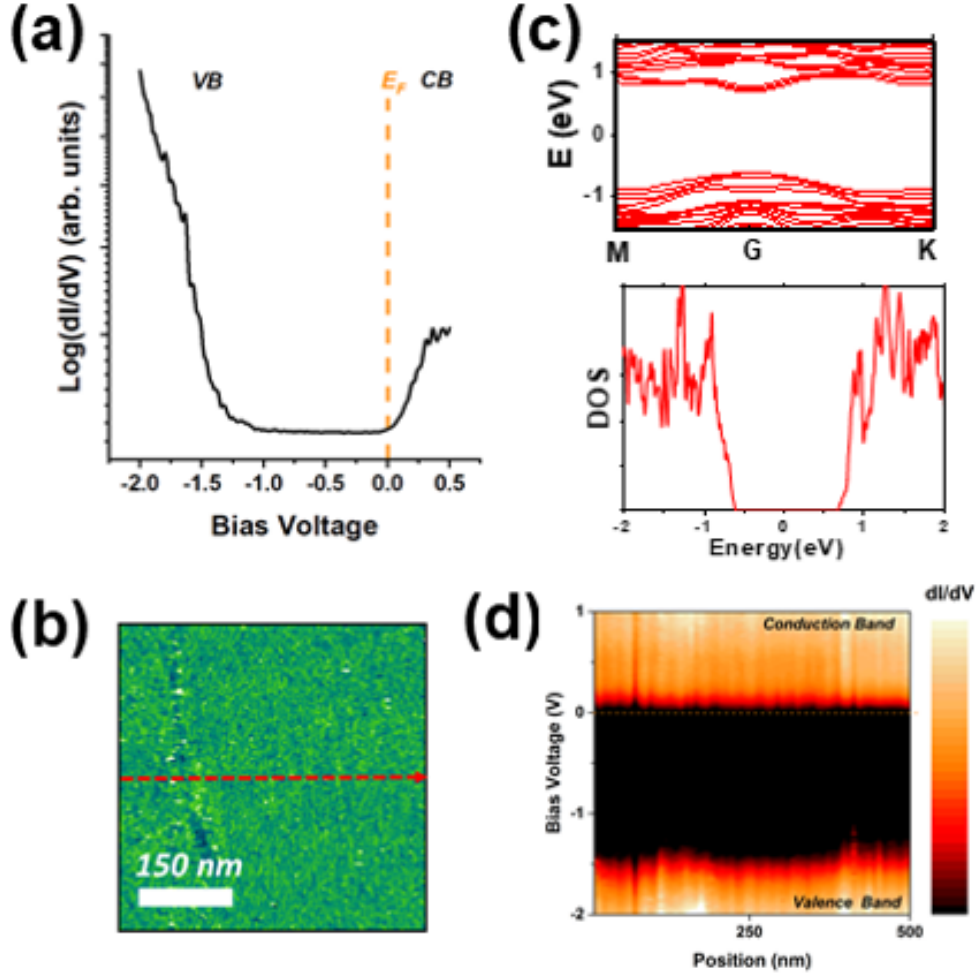


Figure 4.6: (a) Scanning tunneling spectroscopy averaged on the surface of ReS_2 . (b) Topographic image ($V_B = -1.00$ V; $I_T = 65$ pA) of a large area on the ReS_2 surface. (c) Band structure of three-layer ReS_2 and the corresponding DOS. (d) Conductance line map of the scanning tunneling spectra across the dashed line in (b).

We now turn our attention to the band structure of ReS_2 . Electronically, ReS_2 is a semiconductor, however, the nature of the semiconducting gap (direct or indirect) in the bulk versus monolayers remains a subject of discussion both experimentally and theoretically[31, 193–200]. A number of experimental techniques including optical spectroscopy and electronic transport found the bulk band gap to be in the range of 1.40 ± 0.07 eV[31, 171, 173, 191, 201], in agreement with results of theoretical calculations which reported the band gap to be

in the range of 1.4 ± 0.1 eV[31, 170, 172, 174, 176, 195–200]. However, transport and optical spectroscopy are macroscopic measurements which average over large areas of a crystal. Here, we use a local probe to measure the density of states on the surface of ReS₂ crystals. It was found that the differential conductance, in Figure 4.6(a), shows the presence of an energy gap confirming the semiconducting nature of ReS₂. Note that this spectrum, Figure 4.6(a), represents averages over different samples, areas, and tips, and it is plotted on a logarithmic scale[202] for clarity. The variation in the measured band gap values can be seen in Figure 4.7, where the average of all values obtained with a given tip and their standard deviation are represented by points. The average and standard deviation of all STS measurements of the bandgap size are represented by the shaded region, which was extracted from the plot presented in Figure 4.6(a). The extracted value of the energy gap of bulk ReS₂ from this plot is (1.33 ± 0.14) eV, agreeing with previous experiments.

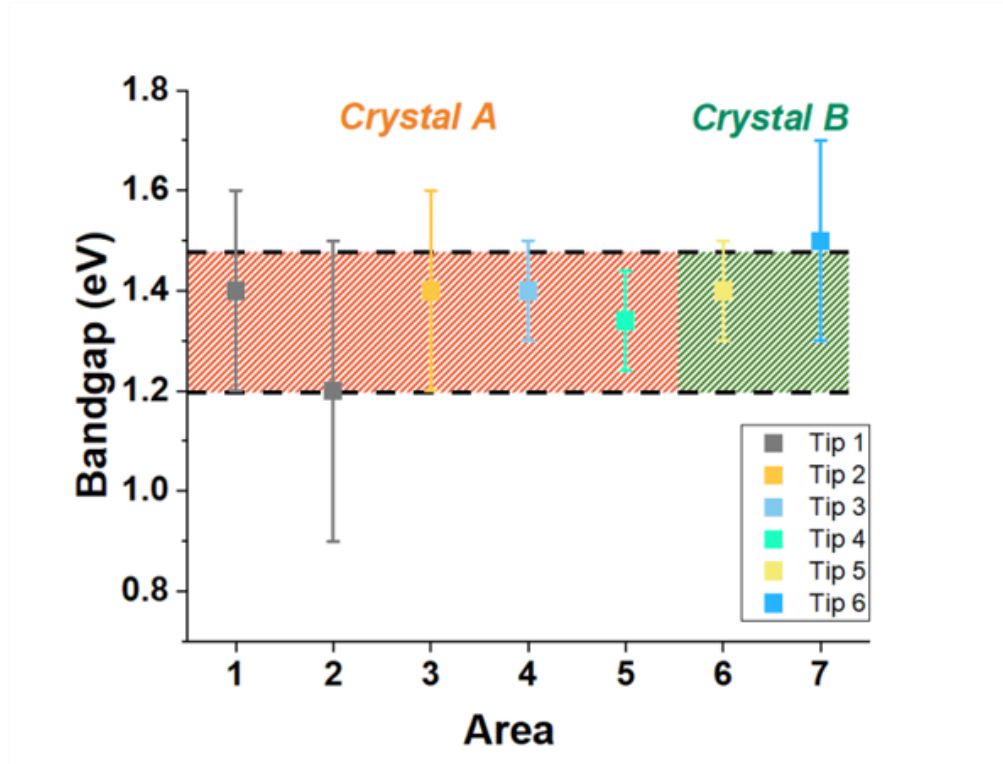


Figure 4.7: Summary of band gap values extracted from measurements on 7 different areas across two ReS₂ crystals (A and B), with a total of 6 different Pt/Ir tips. The error bars represent the standard deviation of the bandgap measured at the respective area of the crystal. The shaded area represents the average and standard deviation of the bandgap from all STS measurements across these 7 areas.

In Figure 4.6(b) we show the spatial variation of the spectrum across the device-size area, topographically presented in the left panel by plotting the scanning tunneling spectra across the dashed line (right panel). Within our resolution, the variation of the energy gap is less than 0.1 eV. These experimental findings are now compared with our theoretical calculations. Figure 4.6(c) shows the band structure and corresponding DOS of a slab of ReS₂ consisting of three layers with details of calculations in the Supplemental Material of [3]. The calculations show a gap at the Γ point, and from the corresponding DOS the energy gap is estimated to be around $E_{gap} = 1.3$ eV, in good agreement with the measured semiconducting energy gap. While the density functional theory (DFT) gap appears to be in good agreement with

the measured semiconducting energy gap, note that it is common for DFT to underestimate the energy gap[203]. Inclusion of many-body corrections at the G_0W_0 quasiparticle level increases the band gap to 2.3 eV. However, the blueshift of quasiparticle transition energies is partially compensated by excitonic effects which reduces the optical gaps to values often consistent with DFT band gaps. In a STS measurement, the zero bias corresponds to the Fermi level (E_F) as indicated by the dashed line in Figure 4.6(a). In an electrically neutral ReS_2 , the position of E_F ought to be in the middle of the semiconducting gap. However, in these samples the position of E_F was closer to the bottom of the conduction band (E_C), indicating the crystal is n-doped.

4.2.2 Characterization of defects in ReS₂

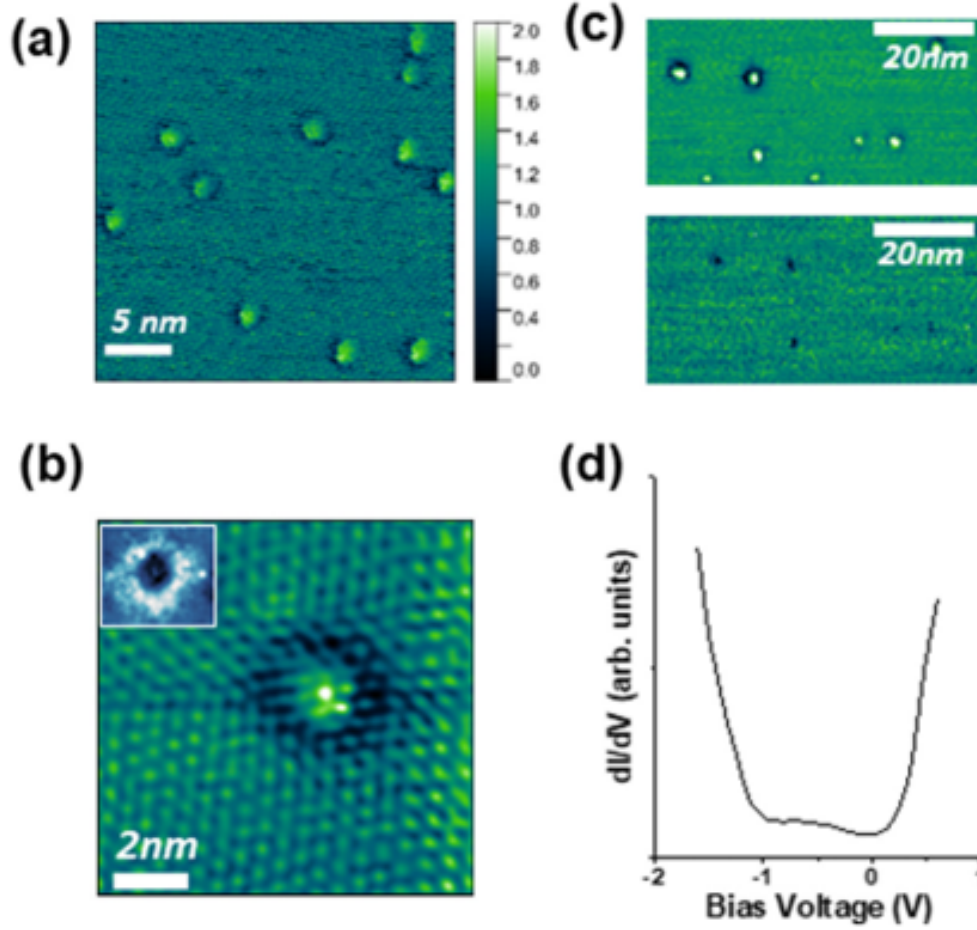


Figure 4.8: (a) STM topographic image ($V_B = -1.20$ V; $I_T = 80$ pA) showing lattice defects. (b) Topographic high-resolution image across a defect. Inset: LDOS map across a defect at $V_B = -1.2$ V and $I_T = 35$ pA. (c) STM topographic images ($I_T = 50$ pA) of the same area at different bias voltages. Top: $V_B = -0.80$ V; bottom: $V_B = +0.80$ V. (d) Averaged STS measured on 22 defects such as the one in (b).

Next, we will focus on analysis of the doping and defects in ReS₂. When imaging the surface of the ReS₂ crystal, we encounter “bright” or “dark” regions representing the presence of a dopant or defect that will electrostatically interact with its environment. Such features have been previously reported on surfaces of doped III–V semiconductors[204], topological insulators[205], transition metal dichalcogenides[4, 206], BP[207, 208], or BN[37]. The most

common type of defects are shown in the STM topographic image of Figure 4.8(a). They have a characteristic bright centre with a dark halo when imaged at negative bias voltages (Figure 4.8(b)). As we vary the scanning parameters, we observe that the apparent height of the defects changes, so that they appear bright at negative bias voltages and dark at positive bias voltages. This is demonstrated in Figure 4.8(c) where we present STM topographic images taken at different bias voltages: -0.80 V and $+0.80$ V respectively. The spectroscopic data acquired on the centre of the defects, presented in Figure 4.8(d) as an average over 22 defects and in Figure 4.11 on only one defect, closely resemble the one on a defect-free area, and reveal the absence of in-gap states. The slight increase in DOS within the gap in Figure 4.8(d) could be due to buried defects under the surface, as previously seen in other TMDs[163].

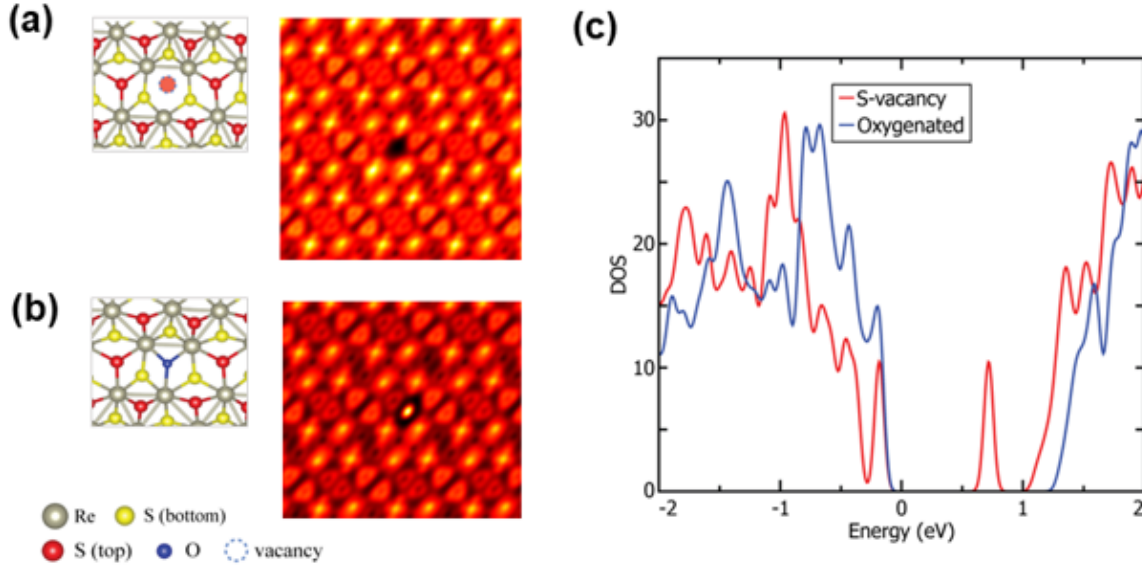


Figure 4.9: Crystal structure and simulated STM images of (a) S vacancy and (b) O absorbed by S vacancy. (c) LDOS of S vacancy and O absorbed by S vacancy.

To complement the STM/STS data, samples of the same crystal were sent for X-ray Photoelectron Spectroscopy (XPS) and, in addition to the expected Re and S[209, 210], we also find the presence of oxygen. The details of the XPS characterization can be found in

the Supplementary Materials of [3].

Different possible atomic-scale defects in the lattice of ReS_2 can have signatures in an STM experiment. For example, point defects, such as a single atom vacancy, single atom adsorption, antisite formation where the S atom is substituted by the Re atom or vice versa, can be formed during the growth of two-dimensional (2D) ReS_2 sheets. To elucidate the possible origins of the most common defects observed in our STM experiments on the surface of ReS_2 , DFT calculations were performed. Simulated STM images of pristine ReS_2 and defected structures, together with their characteristic density of states, are presented in Figure 4.9. The formation of such defects results in dangling bonds within the lattice, which are readily oxygenated under atmospheric conditions, leading to oxygen atom absorption by vacancies within the lattice. In fact, the theoretical results show that oxygen absorption by an S vacancy, as presented in Figure 4.9(b), will create signatures in the density-of-states maps that closely resemble the measured defects, with a distinctive halo structure. Moreover, when we examine the density of states, a S vacancy results in midgap states (red curve in Figure 4.9(c)), while when an O atom is bound to the S vacancy, the semiconducting band gap changes only slightly, in agreement with the experimental finding from STS presented in Figure 4.8(e), strengthening the case for oxygen being a common defect in the ReS_2 layers. These results are consistent with the reports that oxygen is a source of atomic-scale defects in other TMDs[141, 142].

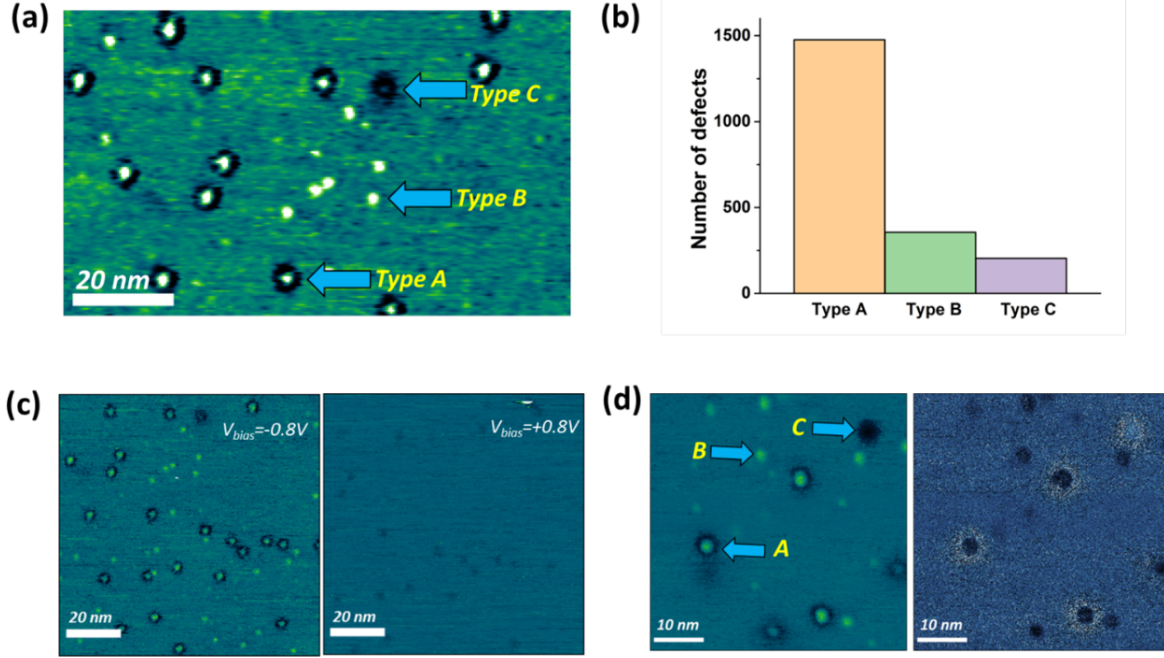


Figure 4.10: (a) STM topographic image ($V_B = -1.20V$; $I_T = 50pA$) with different types of defects labeled A, B, C. (b) Histogram of number of defects of each type encountered by scanning a total area of $4.7 \mu m^2$. (c) STM topographic images ($I_T = 50pA$) of another area taken at indicated bias voltages. (d) STM topographic image (left) ($V_B = -0.86V$; $I_T = 35.0$ pA) and its corresponding dI/dV map at $-0.86V$ (right).

Note that in addition to the Type A defects discussed in Figure 4.8, less frequent occurrences of lattice defects were observed, labeled Type B and Type C. At negative bias voltages Type B defects appear bright, while Type C appear dark. The relative amount of such defects over an area of $4.7 \mu m^2$ is presented in Figure 4.10(b) as a histogram, demonstrating that Type A defects are the most common. Figure 4.10(c) shows the change in contrast for Type A defects when the bias voltage changes sign. The characteristics of the dI/dV maps are also different as shown in Figure 4.10(d).

For the case of the Type A defect shown in Figure 4.11(a), the spectrum on the defect is compared with the spectrum away from the defect (area shown in Figure 4.11(b)) in Figure 4.11(c). Similarly to the average spectrum shown in Figure 4.8(d) earlier in this chapter, no in-gap states appear within spectra acquired at the defect site. This implies that, as with

the WSe₂ defects, these Type A defects in the ReS₂ lattice are likely sulfur vacancies which have had their in-gap states passivated by adsorbed oxygen. This finding is supported by the simulated STM images of various defects (Figure 4.9 and for more, the Supplementary of [3]) wherein the “O adsorbed by S vacancy” strongly resembles the observed qualitative features of the Type A defects.

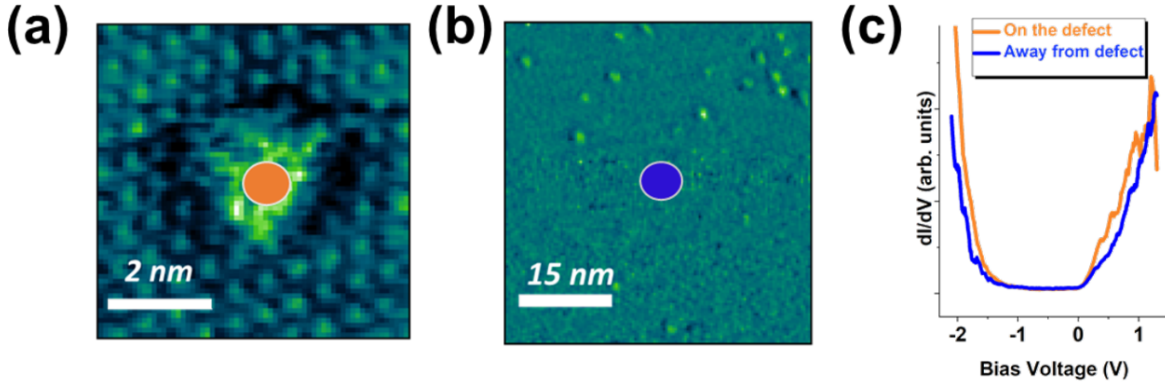


Figure 4.11: (a) STM topographic image ($V_B = -1.20\text{V}$; $I_T = 100\text{pA}$) showing a singular defect. (b) STM topographic image ($V_B = -1.20\text{V}$; $I_T = 100\text{pA}$) of the area near the defect in (a). (c) Average of 20 STS curves measured on the region indicated in orange in (a) (on a defect) and in blue (b) (a region away from defects), demonstrating an absence of in-gap states from the most common, Type A defects.

4.3 Conclusion

In this chapter we revealed the presence of atomic lattice defects and explored their local properties in two bulk, semiconducting TMDs. STM/S characterizations were provided on the nanoscale lattice structure, electronic band gap, and defects of semiconducting WSe₂ and ReS₂. The size, shape, distribution and some of the electronic properties of point defects in WSe₂ were investigated. These details help guide conclusions on devices made from WSe₂ whose properties may depend on presence of defects. In ReS₂, by comparing the signatures of defects in the STM/STS experiment with the theoretical calculations, oxygen was identified as being frequently absorbed at defect sites. The same conclusion could be inferred based on

the results on WSe₂, though the auxiliary characterization techniques which reinforce that conclusion were not repeated on WSe₂. As the nature of atomic defects is critical in understanding the properties of 2D materials, these results pave the way toward understanding and engineering properties of 2D semiconductors.

Chapter 5

Mixed-symmetry van der Waals heterostructures

Parts of this chapter follow closely or partly reproduce text from the published paper, “Ryan Plumadore, Mohammed M. Al Ezzi, Shaffique Adam and Adina Luican-Mayer, *Moiré patterns in graphene–rhenium disulfide vertical heterostructures*. (2020) Journal of Applied Physics 128, 044303”. The Declaration of Authorship at the beginning of this thesis (*pages iii-iv*) lists the contributions of each author to this work in detail.

In this chapter, details on the characterization of a 2D van der Waals heterostructure consisting of monolayer graphene on multilayer ReS₂ are presented. The goal was to image and characterize the effects of a moiré pattern formed between the lattices of different symmetry of graphene (hexagonal) and ReS₂ (triclinic), shown in Figure 5.1(c). Room temperature STM/S is used to visualize the surface and its heterogeneity at the atomic scale, and to measure the band structure of the system. The sample from which results are shown is representative of the results obtained using the finalized procedure, described in Chapter 3. This technique was developed in the process of making ReS₂/graphene heterostructures. As a result, some samples did not undergo the now-standard AFM brooming step used to clean the final surface prior to measurement. Instead, a modified and more aggressive annealing procedure was utilized (300°C in H/Ar forming gas for 10H; 300°C in vacuum at 1E-9 Torr

for 10H). On such samples, AFM was used only in tapping mode to measure topography (Figure 5.1(b)), in order to assist with locating regions of interest on samples later in the STM. In Figure 5.1(b), bubbles and ridges between the graphene and ReS_2 layers are visualized white features on the heterostructure. It should be noted that while clean samples prepared without AFM brooming are achievable, the yield is much improved by the AFM brooming technique.

5.1 Fabrication of graphene/ ReS_2 heterostructure

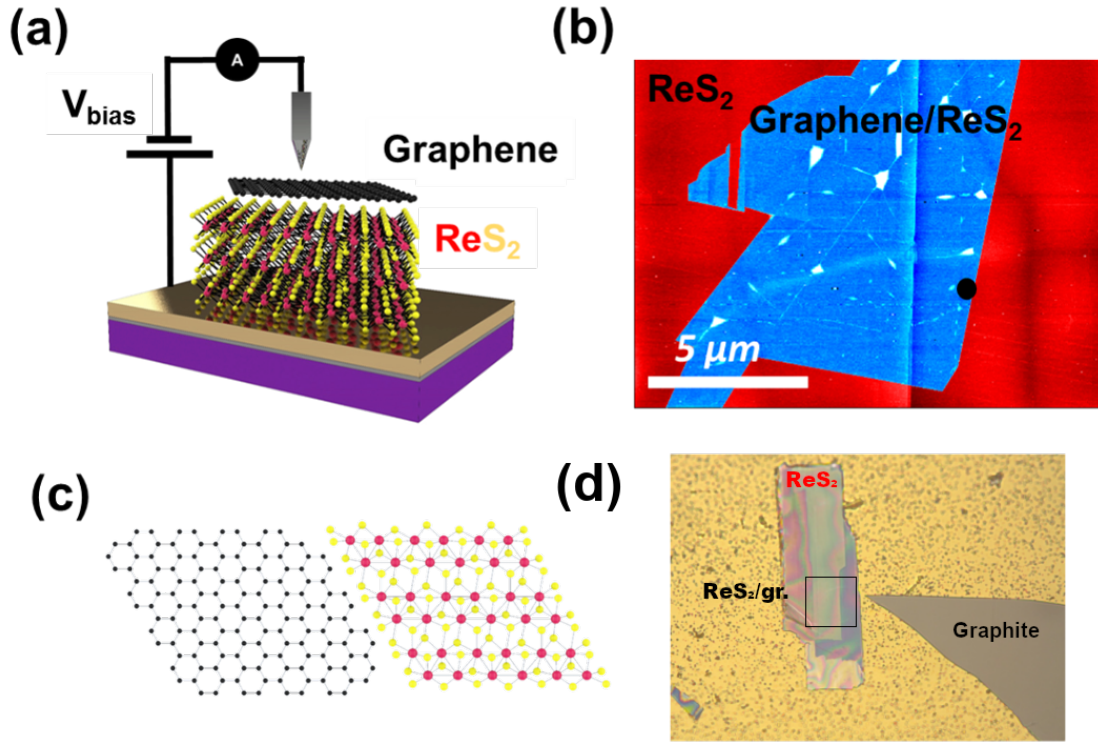


Figure 5.1: (a) Schematic of the STM experiment on a ReS_2 /graphene heterostructure. (b) Atomic force micrograph of the area where graphene is stacked onto ReS_2 . The black dot indicates the region where the data in Figure 5.2 were taken. (c) Graphene and ReS_2 lattices. (d) Optical microscope image of the ReS_2 /graphene heterostructure.

The fabrication procedure is described in Chapter 3, though a notable modification was made here. During fabrication, a large piece of graphite was transferred simultaneously

with the device and placed nearby. This flake facilitated the process of landing the STM tip and locating the sample, as the graphite flake was selected such that it had obvious features pointing to the location of interest on the sample. For example, the device shown in this thesis was accompanied by an arrow-shaped graphite flake (seen on the right of Figure 5.1(d)), which points to section of the bulk ReS₂ flake covered by the graphene monolayer. By landing on the large graphite flake and following its edge, the region of interest on the sample could be located quickly.

5.2 Characterization of the graphene/ReS₂ device

The same bubbles and ridges present in the topographic AFM images, seen in Figure 5.1(b), can be visualized in the STM topography - by following these features, the graphene/ReS₂ edge is identified (Figure 5.2(a)). A step height of (0.45 ± 0.01) nm was measured across the edge, consistent with an atomically clean interface between the two layers. The typical height of the bubbles is 10–20 nm and their typical width is 80 nm. This aspect ratio is consistent with previous reports [211] and reflects the specific adhesion energy of the two layers.

In Figure 5.2(b), we show the averaged scanning tunneling spectra over areas in Figure 5.2(a), both on the graphene/ReS₂ heterostructure as well as on the bare ReS₂. On the graphene, we observe the characteristic spectrum[212], minimally doped away from the Dirac point. This doping level is consistent with previously reported experiments where graphene was placed on TMDs including MoS₂ or WSe₂[213]. On the ReS₂, the spectrum reveals the semiconducting gap, where we indicate the valence band (VB) and conduction band (CB). The measured value of the gap is $\Delta E_{ReS_2} = 1.2\text{eV} \pm 0.2\text{eV}$, consistent with previous reports[31, 174, 175, 214, 215]. The finite density of states within the semiconducting gap is possibly due to the presence of defects buried in the ReS₂ crystal[214]. Note that in STS measurements, the Fermi level is at zero bias voltage, as indicated in Figure 5.2(b).

It was found that in this system, graphene's Dirac point was aligned with the conduction band edge of ReS_2 . This is also consistent with the band alignment measured for MoSe_2 and WSe_2 heterostructures[216]. Previous reports of graphene/TMD heterostructures found graphene's density of states to be unaltered by the presence of a substrate[78]. However, in the presence of disorder, features in the scanning tunneling spectrum of graphene were attributed to scattering due to the presence of defects in the TMD[213]. This is consistent with the observation that, in the graphene/ ReS_2 heterostructure reported here, the graphene spectrum deviates from the standard V-shape above the Dirac point, likely due to the presence of defects in the ReS_2 lattice.

Figure 5.2(c) shows a topographic image acquired in the dashed area of Figure 5.2(a) where the sharp edge of the graphene is visible[217]. On the ReS_2 , we can resolve the atomic lattice, attesting to the cleanliness of the sample surface, and observe the same defects reported in Chapter 4, as marked for example by the arrow in 5.2(c). At the same boundary, using differential conductivity maps, we spatially resolved the local density of states at the indicated bias voltages in Figure 5.2(d). The electronic contrast between graphene/ ReS_2 and ReS_2 is most pronounced at -800 mV, -500 mV, and -200 mV, consistent with the spectroscopic data. At energies corresponding to the conduction band of ReS_2 , the contrast between the ReS_2 /graphene and the bare ReS_2 is minimal.

5.3 Observation of a moiré superpattern between graphene and ReS_2

A characteristic topographic feature that the STM topographic images reveal in this system is presented in Figure 5.3(a), where we observe the appearance of a superpattern of parallel stripes. A height profile across the dashed line is plotted in Figure 5.3(b). The height corrugation of the pattern is approximately 200 pm, consistent across several areas measured

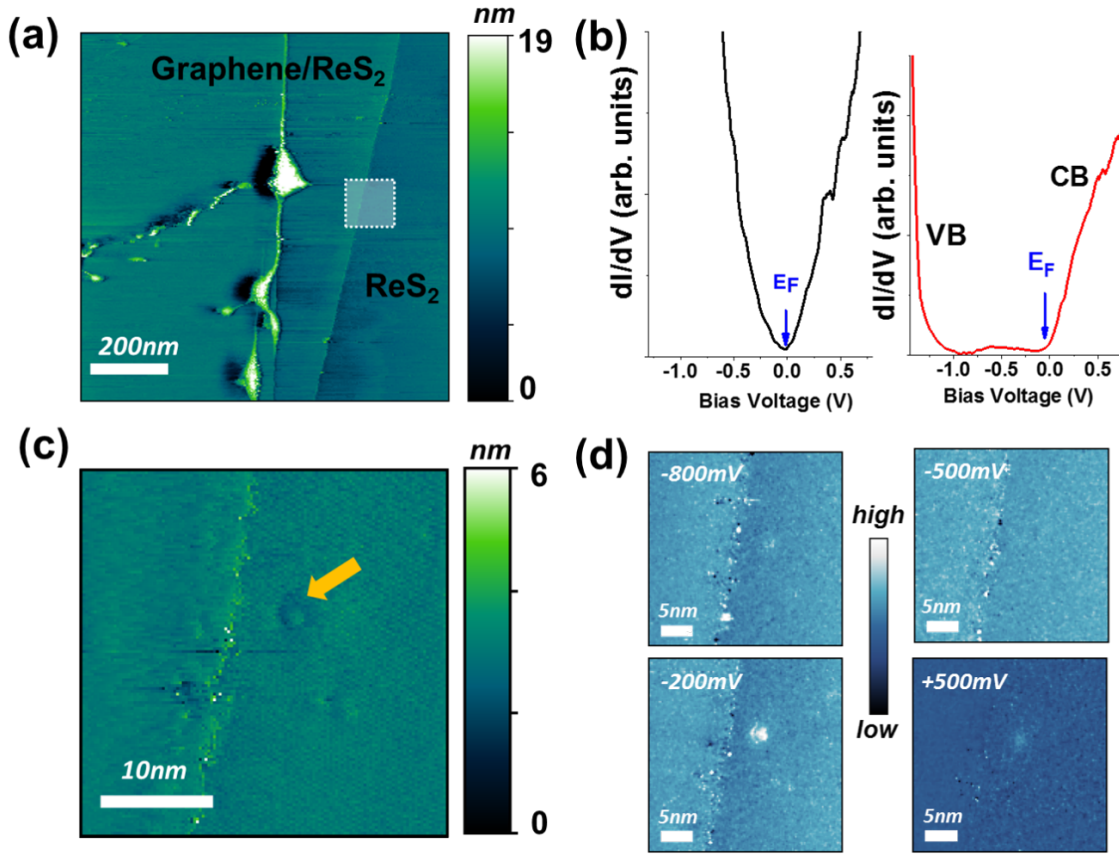


Figure 5.2: (a) STM topographic image of an area at the boundary between the ReS_2 covered with graphene and ReS_2 ($V_B = -0.5$ V; $I_T = 200$ pA). (b) Scanning tunneling spectroscopy on the graphene (left) and ReS_2 (right) ($V_B = -0.5$ V; $I_T = 100$ pA). (c) Topographic image at the boundary between graphene and ReS_2 ($V_B = -0.2$ V; $I_T = 110$ pA). The arrow indicates the presence of a defect in the ReS_2 lattice. (d) Conductance map in the same area as (c) taken at indicated bias voltage.

on different samples and with different tips. The higher resolution topographic map shown in Figure 5.3(c) was taken across the area indicated in Figure 5.3(a) by the white square; the atomic lattice of graphene as well as the striped pattern are visible. This superpattern of stripes resembles the features reported in both the graphene/BP and graphene/ ReSe_2 systems[15, 218]. Unlike in those systems, the period of the superpattern observed is constant across different areas, samples, and tips. This suggests that either the measured structure corresponds to an energy minimum for the twist at the graphene/ ReS_2 interface, or, that

moiré patterns corresponding to other angles are less pronounced and therefore difficult to measure within the resolution of our STM. Indeed, theoretical calculations for the case of graphene/BP found that due to anisotropic orbital hybridization at the interface, the strength of the interlayer interaction could be orientation dependent[15]. Another feature observed in similar systems exhibiting periodic superpatterns is the presence of strain, which in graphene can lead to the presence of pseudo-magnetic fields and associated quantized energy levels[15, 219, 220]. In our experiments, we have not observed signatures of such effects in the spectroscopic data at room temperature.

The experimentally observed one-dimensional stripes seem to be moiré patterns resulting from the interference pattern between graphene and ReS₂. Graphene has a hexagonal lattice with lattice parameters $a_1 = a_2 = 0.246$ nm, while ReS₂ has a triclinic lattice with $b_1 = 0.651$ nm and $b_2 = 0.641$ nm and the angle between b_1 and b_2 is 118.9°. Generally, for two materials with different crystal structures, the moiré patterns emerge due to the interference of extended unit cells of both materials and a possible relative twist angle between them[221].

In this case, the extended unit cells for graphene and ReS₂ should have primitive vectors given by $(m \times a_1, n \times a_2)$ and $(p \times b_1, q \times b_2)$ with a possible relative twist angle θ between them, where m , n , p , and q are four integers to be determined. To find the size of these effective unit cells and their relative twist angle, the calculations are carried out in reciprocal space. The reciprocal lattice vectors for graphene are given by $G_{mn} = mG_1 + nG_2$, where G_1 and G_2 are the primitive reciprocal vectors for graphene. Similarly, the reciprocal lattice vectors for ReS₂ are $S_{pq}(\theta) = pS_1(\theta) + qS_2(\theta)$, where S_1 and S_2 are the primitive reciprocal vectors for ReS₂. The angle dependence is used to allow for a relative twist angle between the two materials. The real space wavelength characterizing the periodicity of the moiré patterns can be linked to reciprocal space quantities by

$$\lambda_{mnpq}(\theta) = |K_{mnpq}(\theta)|^{-1} \quad (5.1)$$

where $K_{mnpq}(\theta)$ is the difference between the wave vectors of both materials and is given by

$$K_{mnpq}(\theta) = G_{mn} - S_{pq}(\theta) \quad (5.2)$$

To find the possible moiré patterns, we utilize Eq. 5.1 and search for patterns that resemble the experimentally observed patterns.

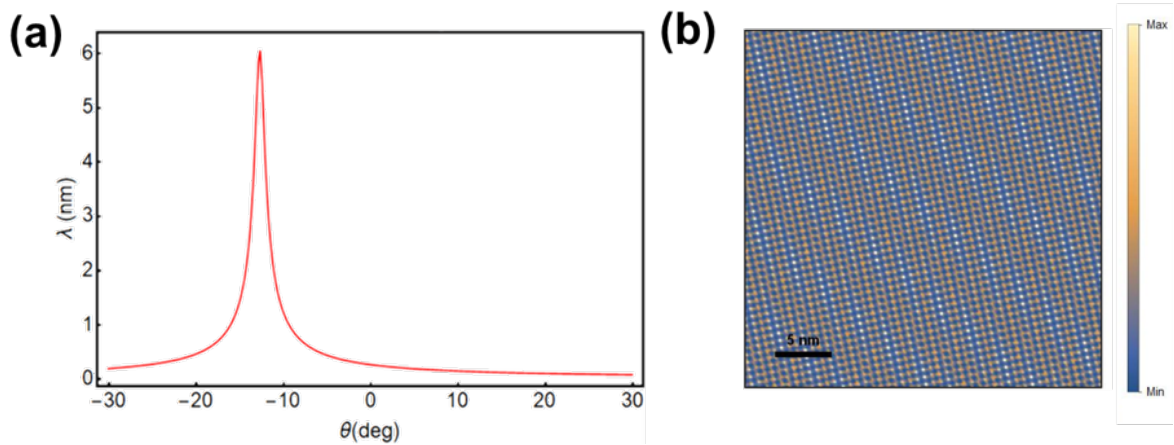


Figure 5.4: (a) Numerical calculation of moiré pattern wavelength as a function of twist angle. (b) Simulated real space image of the moiré pattern at a twist angle of 12° and with periodicity ~ 5.2 nm.

Our search in reciprocal space leads to the conclusion that the striped pattern is due to the extended unit cells with parameters $(m, n, p, q) = (3, 1, 6, 5)$. The moiré wavelength as a function of twist angle is shown in Figure 5.4(a). We can see the existence of a window of twist angles centred around 12° where the wavelength is approximately 5 nm. Based on this calculation, it is reasonable to estimate the angle of rotation between the graphene and ReS_2 to be about 12° . For most angles, the superpattern is predicted to have a period of below 1 nm, which becomes comparable to the size of the ReS_2 lattice parameters and could be less pronounced in the STM topographic images. This is consistent with the fact that measured superpatterns on the sample are larger (around 5 nm) and only present in some areas of the sample. Figure 5.4(b) shows a simulated image for the moiré pattern in real space where the

one-dimensional stripes can be seen with a periodicity of approximately 5.2 nm, and indeed this image strongly resembles Figure 5.3(c).

5.4 Conclusion and Discussion

In this chapter, we examined monolayer graphene on bulk ReS_2 , assembled via the inverted dry-transfer method, presented in Chapter 3. Through this method, van der Waals heterostructures can be assembled with pristine surfaces and interfaces by completely avoiding contamination with polymers, unlike in traditional stacking techniques. Scanning tunneling microscopy and spectroscopy on the graphene/ ReS_2 device were used to gain insight into the local electronic variations due to the interlayer interactions. We found a characteristic striped superpattern and discussed its origin as a moiré pattern between the two lattices. This work sheds light on the complex interfacial effects in novel heterostructures of two-dimensional materials with different lattice symmetries.

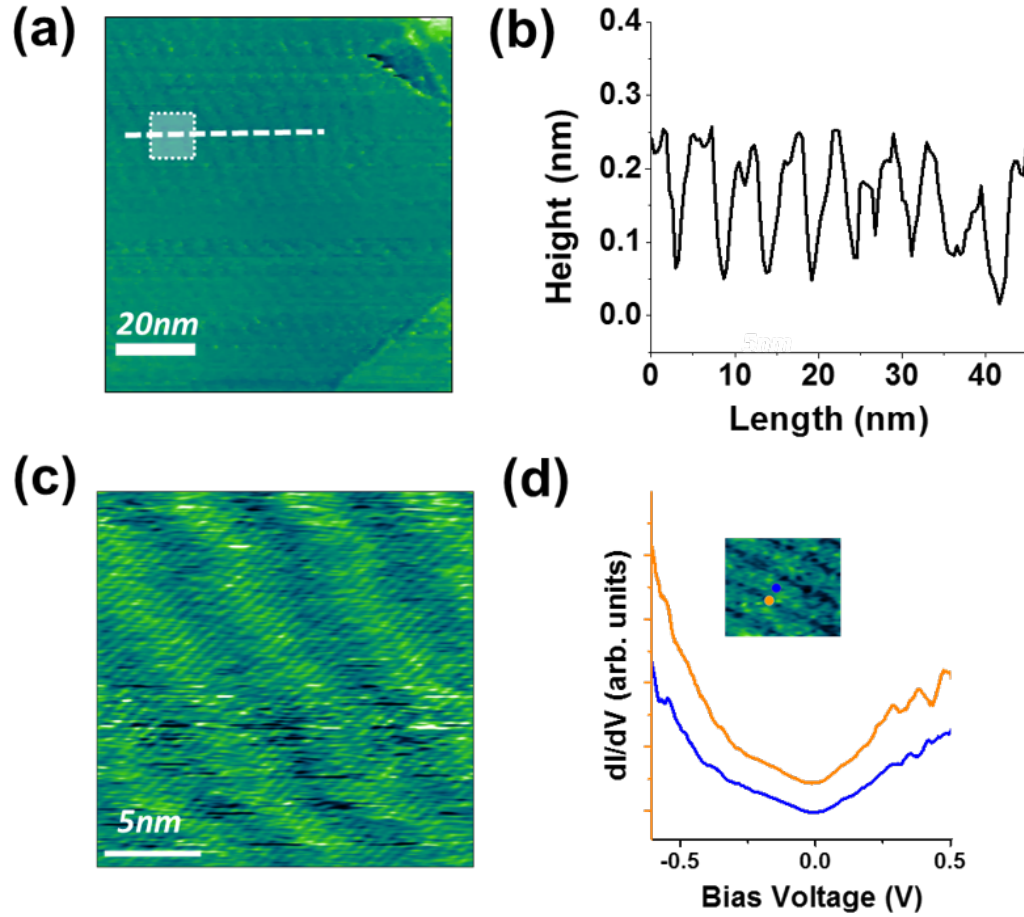


Figure 5.3: (a) Striped superpattern observed across the graphene/ReS₂ interface in an STM topograph ($V_B = -1.0$ V; $I_T = 100$ pA). (b) Height profile measured across the line indicated in (a). (c) Higher resolution STM topographic image corresponding to the area indicated in (a) ($V_B = -1.0$ V; $I_T = 100$ pA). (d) STS on the peaks and valleys of the striped pattern as indicated in the inset.

Chapter 6

Topological van der Waals materials

Parts of this chapter follow closely or partly reproduce text from an unpublished manuscript in preparation, “Ryan Plumadore, Leena Aggarwal, Yanglin Zhu, Yingdong Guan, Zhiqiang Mao, Adina Luican-Mayer, *Visualizing the heterogeneity of the surface and edge states in magnetic topological insulator $MnBi_2Te_4$* .”. The Declaration of Authorship at the beginning of this thesis (*pages iii-iv*) lists the contributions of each author to this work, to-date, in detail.

$MnBi_2Te_4$ was proposed as the first intrinsic antiferromagnetic 2D topological insulator (TI)[42, 98, 222–227], a claim which has since been confirmed by numerous angle-resolved photoemission spectroscopy (ARPES) results which observed the exchange gap in the bulk band structure [42, 98, 223, 228–230]. Magnetic measurements confirmed the Mn ions in each unit cell have a high ($S=\frac{5}{2}$) spin with a large magnetic moment of $\sim 5\mu_B$ [98], and gave the first signs of the antiferromagnetic transition that occurs around $T = 24K$. Soon afterwards, thin films of $MnBi_2Te_4$ were shown to exhibit the anticipated topological phases: gate-tunable and reversible quantum anomalous Hall (QAH) devices [231], QAH in the absence of magnetic field in odd-number thin layers [227], and even-number thin samples hosting axion insulator states[232–236].

The structure of $MnBi_2Te_4$ can be considered as a Mn-Te layer inserted into the Bi_2Te_3 tetradymite structure common to the well-known topological insulators. This rhombohedral

structure consists of van der Waals bonded quintuple-layers, alternating between Te and Bi sub-layers. With the additional Mn-Te inserted, the structure becomes a septuple-layer, in the sequence Te-Bi-Te-Mn-Te-Bi-Te.

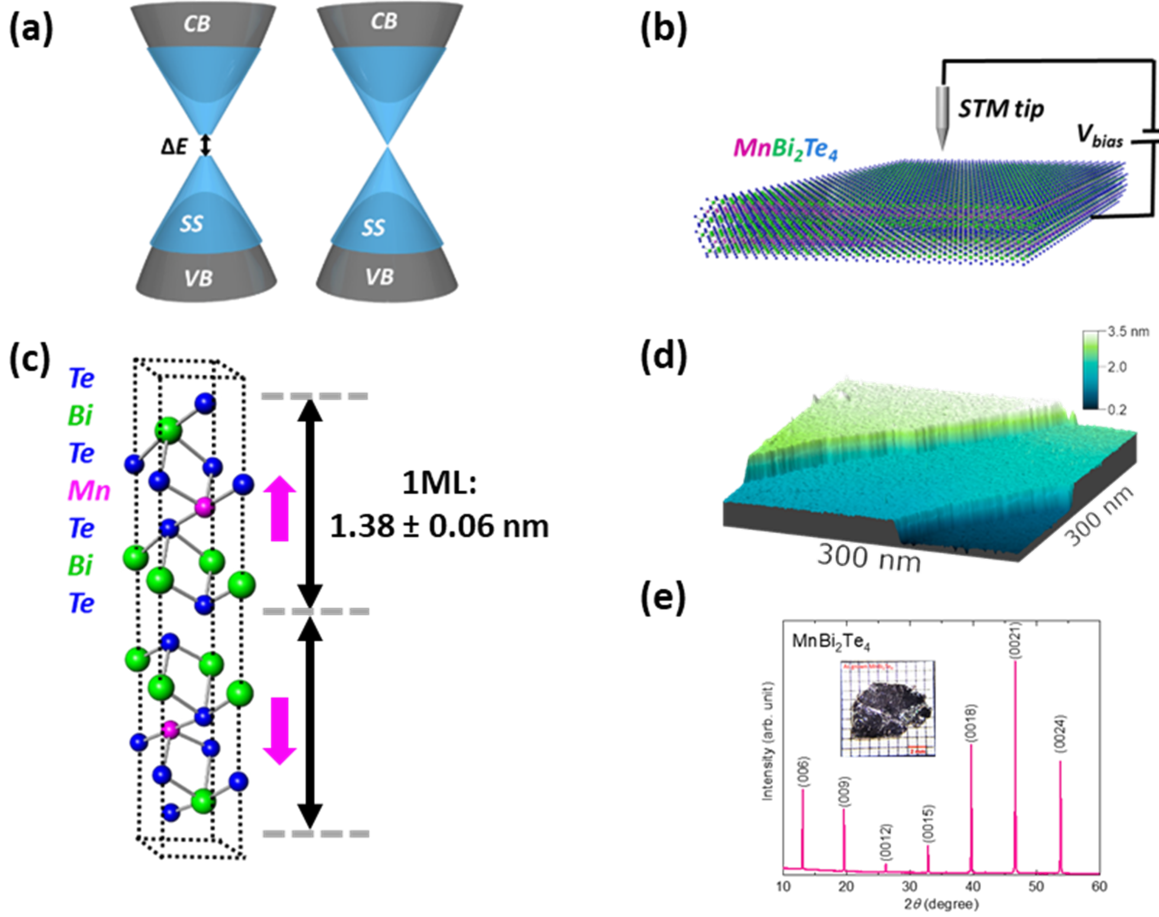


Figure 6.1: (a) Schematic representation of a band structure with bulk energy gap and a gapped (left) and non-gapped (right) surface state. (b) Schematic of the scanning tunneling microscopy experiments on the surface of MnBi_2Te_4 . (c) Side-view of the unit-cell crystal structure of MnBi_2Te_4 , including spin. (d) 3D topographic map ($V_B = 500 \text{ mV}$; $I_T = 150 \text{ pA}$) of typical single-layer step edges on the MnBi_2Te_4 surface. (e) XRD data, acquired by Yanglin Zhu and Yingdong Guan, showing the peaks and indicating the crystalline phase of the crystal.

The schematic in Figure 6.1(a) represents the typical band structure of TIs, where characteristic gapless surface states in the absence of magnetic elements form a Dirac cone.

MnBi_2Te_4 is a topological insulator with intrinsic magnetism, which breaks time-reversal symmetry due to the spin-orbit coupling of Te atoms which modifies the d-orbitals of the nearby Mn atoms.[237, 238] The magnetic properties are provided mainly by the 3d states of the Mn atoms, while the topologically nontrivial properties are dominated by the p states of the Bi and Te atoms.[239] Therefore the surface states, which typically are gapless in a non-magnetic TI, acquire an exchange gap. The surface state Dirac fermions become massive and a gap ΔE opens at the Dirac point, as suggested in the left part of Figure 6.1(a). The long-range ferromagnetic intralayer coupling, antiferromagnetic interlayer coupling, and magnetic anisotropy with out-of-plane easy axis have all been confirmed experimentally by inelastic neutron scattering[240–242]. The exchange gap is crucial for the formation of novel phases, as well as for the realization of proposed ones, such as flat-band condition in twisted MnBi_2Te_4 [243], ferromagnetic interlayer coupling[244], heterostructures realizing QAH effect at higher temperatures[245], devices incorporating topological edge states for low-power-consumption electronics and spintronics, [235, 236] and many novel magnetic topological states including ferromagnetic Weyl semimetals, high-order topological insulators, and unusual kinds of QAH insulators[238].

However, the presence and magnitude of this gap are still to be understood. Recently, it was claimed that the previously reported surface gap in MnBi_2Te_4 single crystals was actually related to the bulk gap of the material, which survives at temperatures larger than the antiferromagnetic transition temperature ($T_N = 25\text{K}$) in MnBi_2Te_4 . [42, 98, 225, 226, 229, 231, 246, 247] Some ARPES measurements have shown that MnBi_2Te_4 has gapless surface states within the bulk band gap which remain unchanged across the Néel temperature, suggesting a more complex scenario in which competing structural and magnetic orders could be sensitive to material imperfections.[224, 247–249] These states are believed to result from a combination of 1) magnetic impurities or defects, for example, random Mn-Bi substitutions

at Bi sites which locally disrupt the otherwise uniform surface magnetism[250–252], 2) surface relaxations with the formation of magnetic domains of nanometer size [223, 224, 248, 249, 253], and 3) modifications in the crystalline structure during sample cleaving resulting in re-orientation of the magnetic moments of Mn atoms[251, 254]. The delicate interplay between these factors and the intrinsic surface magnetism in MnBi_2Te_4 , which is required to break the time-reversal symmetry protecting the robust surface states, have thus far hindered observations of the gapped system. To develop a comprehensive understanding of this class of materials, and ultimately achieve control over their topological phases, more experimental characterization of the spatial heterogeneity of magnetic topological insulating systems is needed.

6.1 Surface characterization of MnBi_2Te_4

In this chapter, bulk MnBi_2Te_4 single crystals are characterized by low temperature ($T = 10$ K) scanning tunneling microscopy and spectroscopy, with the aim of studying the spatial variation of their local electronic properties. The crystal structure of MnBi_2Te_4 is shown in Figure 6.1(c). It has a trigonal structure, belonging to the space group $R\bar{3}m$, with septuple-layer units weakly bonded out-of-plane by van der Waals forces. Bulk MnBi_2Te_4 crystals were prepared following the in-situ cleaving procedure described in Appendix 8.3.1. This ensures the freshly cleaved surface only experienced an inert nitrogen environment, and only for a short time, before being introduced to vacuum and subsequently moved to the STM for study. In this way, the formation of an oxide layer or of surface reconstructions are mitigated. All STM measurements were performed using cut Pt-Ir tips. Topographic images were taken in constant-current mode and spectroscopic signals were recorded with AC modulation of 3-10 mV and with a reference frequency of 1.325 kHz.

Figure 6.1(d) shows a 3D projection of a measured STM topography of the MnBi_2Te_4

crystal surface, with each step height consisting of one layer of the septuple-unit. The difficulty of synthesizing large, single crystalline samples of MnBi_2Te_4 has been noted in the literature[42], and reports on growth of MnBi_2Te_4 have indicated the presence of other crystal phases,[255] including minor phases of Bi_2Te_3 and MnTe [256], collapse and reconstruction of exfoliated crystals to Mn-doped Bi_2Te_3 and a $\text{Mn}_x\text{Bi}_y\text{Te}$ double layer [254], as well as the presence of various defects in the lattice [42]. To verify phase purity and quality, crystals were characterized by X-Ray powder diffraction as shown in Figure 6.1(e). ARPES on crystals grown from the same source, though from different batches, revealed the presence of a gap [229]. Even still, the defect concentration in MnBi_2Te_4 has been demonstrated to be non-uniform, varying across samples from the same batches and even within the same samples at different cleavage sites,[250] a result which is supported by the current study. In the experiments presented here, areas with higher-than-average defect concentration were identified (see Fig. 6.2), when compared to the more typical topography shown in Figure 6.3.

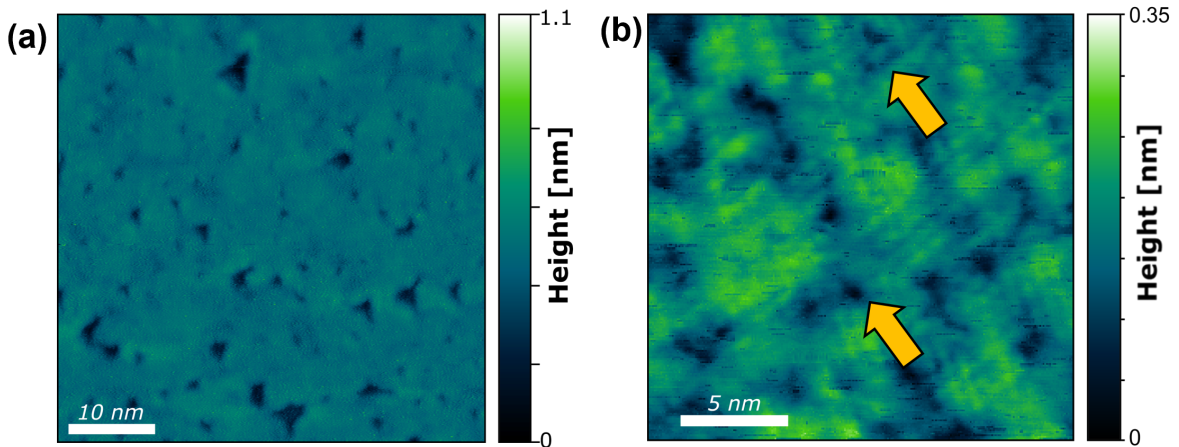


Figure 6.2: (a) STM topography of MnBi_2Te_4 surface with higher than average defect density ($V_B = 500$ mV; $I_T = 40$ pA), showing primarily triangular defects. (b) STM topography of an area with atomic resolution, where both circular point defects and triangular defects are visible ($V_B = -500$ mV; $I_T = 80$ pA).

In order to characterize the variation of the surface states in MnBi_2Te_4 , measurements

were repeated at several spatially separate areas and at different cleavage sites of the crystal, as well as with different tips. In this way, we can use the STM to get an understanding of how spatially uniform the local electronic structure is, on the macroscopic scale. Both gapless and gapped surface states were found, both of which were uniform across large areas in the same MnBi_2Te_4 crystals. The presence of strong spin fluctuations on the surfaces is related to topologically gapped surface states [98, 229]. Furthermore, the realization of localized 1D edge mode in even- and odd-numbered layers in the bulk gap suggests the existence of axion and QAH phases, respectively, in MnBi_2Te_4 . These phases have been reported earlier in MnBi_2Te_4 thin films [234]. Our results give direct evidence of the presence of these topological phases in bulk MnBi_2Te_4 .

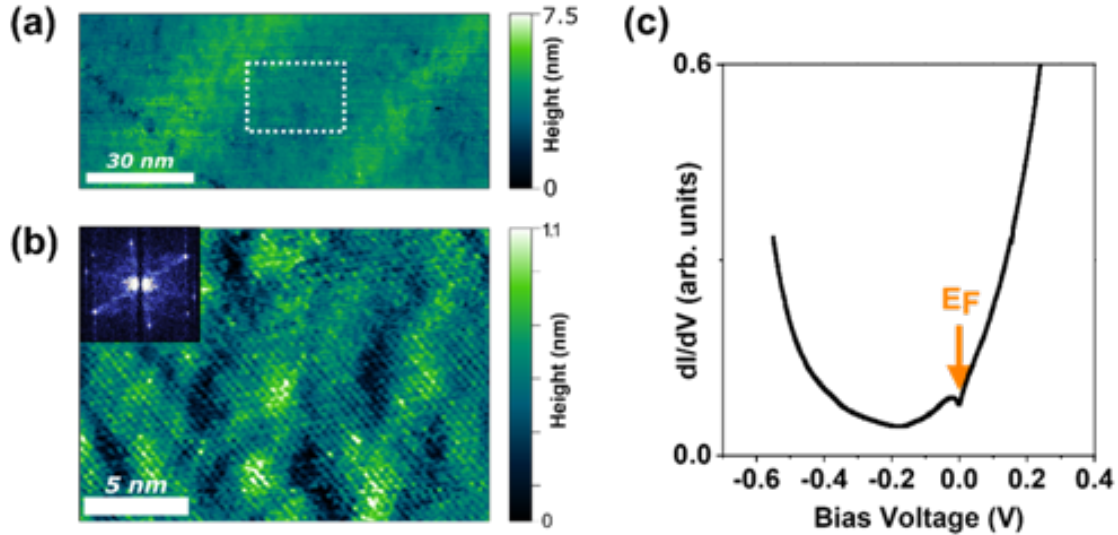


Figure 6.3: (a) STM topography and spectroscopy of MnBi_2Te_4 single crystal: (a) Topographic image of the MnBi_2Te_4 surface and (b) atomic resolution obtained within the area of the white dotted box in (a), with scanning parameters: $V_B = 1000$ mV; $I_T = 100$ pA. Inset: Fast Fourier transform of the image. (c) Average dI/dV spectroscopy over the surface in (a), taken at $V_B = -400$ mV; $I_T = 75$ pA.

Figure 6.3(a) shows STM topography of a device-sized area of MnBi_2Te_4 , where the contrast originates in the top-most layer of Te atoms. Figure 6.3(b) shows an atomic resolution STM image, acquired from the area in the white box of Figure 6.3(a). The measured hexago-

nal lattice with lattice constant of (0.45 ± 0.05) nm is characteristic of the top Te-layer [250, 257].

6.2 Topological surface gaps in MnBi_2Te_4

In Figure 6.3(c), spectroscopy acquired over the area in Figure 6.3(a) shows the common spectroscopy found on most surfaces of the MnBi_2Te_4 crystal. The spectroscopic features are dominated by the topological gapless surface states with Dirac point at the Fermi level. Similar gapless surface states, as measured by STS, have been reported previously in the literature, where a non-uniform magnetic field was attributed to the presence of surface defects. [241, 250, 251, 257] Other areas of the MnBi_2Te_4 crystals in this report had defects resembling those presented in the literature.

Next, the variation of the spectroscopic features across different areas from the same MnBi_2Te_4 crystal was examined, as shown in Figure 6.4. Most areas showed a similar gapless topological surface state, with a Dirac point feature at the Fermi level. Figure 6.4(a,b) shows an area which resembles the most common spectrum presented in Figure 6.3(c), yet with progressively more reduced signal across energies from the valence band and across to the Fermi level. In some areas (Figure 6.4(c,d)) the valence-band edge shifts, leading to a symmetric band structure which is reminiscent of that seen in ARPES reports, [223, 228–230, 247] and where the density of states is reduced even further at the minimum point. The observed shift in the valence band edge and different band gap sizes may be attributed to local surface reconstruction and surface defects [241, 251]. All observed spectra have very low density of states in this minimal section around the Fermi level, on the order of $\sim \text{pA}$ or less, even in the presence of defects. There is a possibility that these surfaces could exhibit a gap, yet due to intrinsic non-uniform magnetic fluctuations caused by defects or other surface reconstructions, some surface states persist.

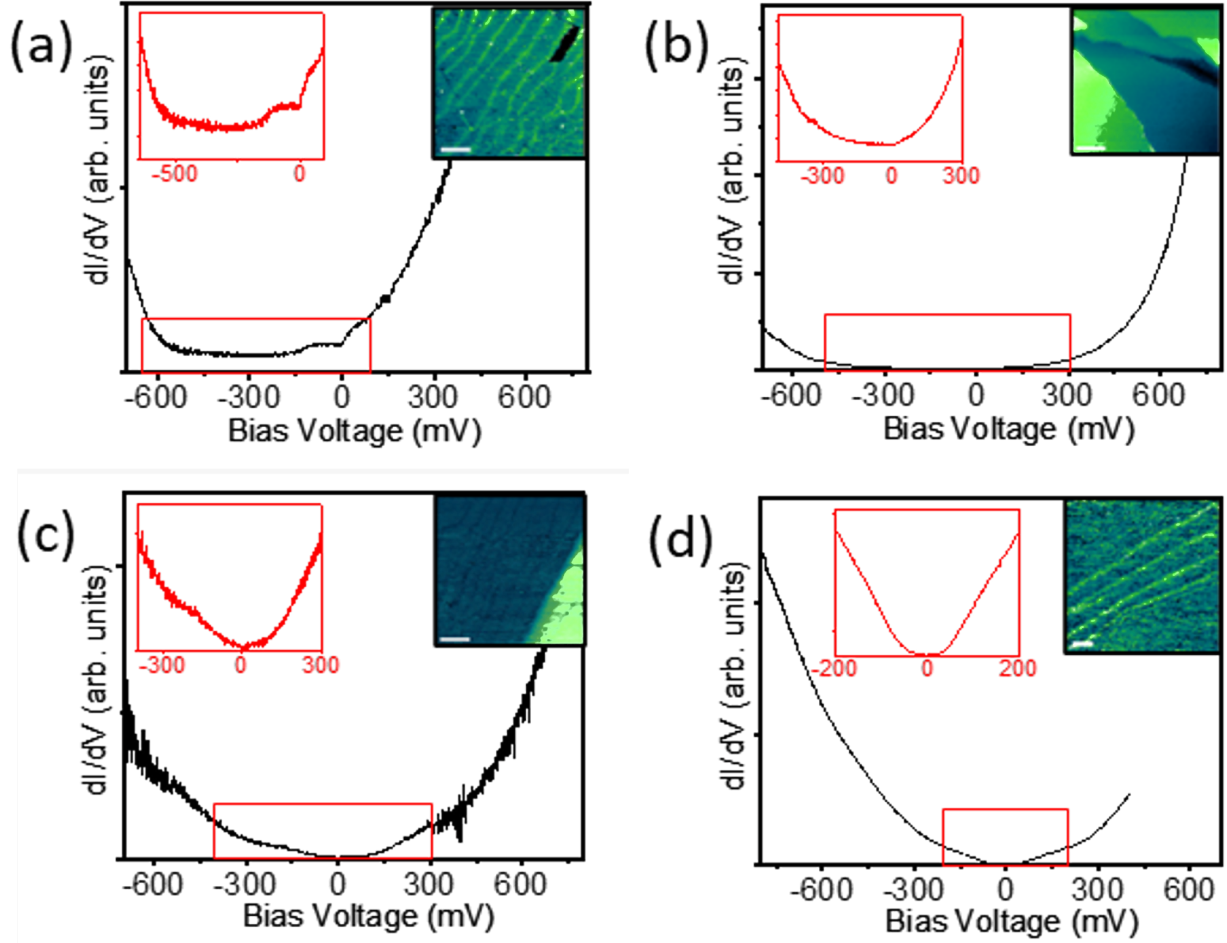


Figure 6.4: dI/dV spectroscopy of different areas from the MnBi_2Te_4 sample, taken with tunneling junction resistance in the range of 1.25-5.34 $\text{G}\Omega$. Inset, Left: Zoom in on the energies indicated by the red boxes, around the minimum intensity of each spectrum. Inset, Right: STM topography from the area where spectroscopy was acquired. Scanning parameters for each scan were: (a) $V_B = 500$ mV and $I_T = 400$ pA, inset scalebar: 100 nm, (b) $V_B = 500$ mV, $I_T = 400$ pA, inset scalebar: 200 nm, (c) $V_B = 400$ mV, $I_T = 150$ pA, inset scalebar: 100 nm, and (d) $V_B = 500$ mV, $I_T = 200$ pA, inset scalebar: 100 nm.

Despite this potential scenario, in some areas the emergence of a true band gap across the Fermi level is observed (Figure 6.4(c,d)), where the density of states is reduced fully to zero. The value extracted for the band gap in these areas falls within the range of $95 \pm 9 \text{ meV}$. In areas with larger (partial) gaps, such as in Figure 6.3(b), note that the gap widens primarily towards the valence band side and begins to resemble the gapless spectroscopy. The band gap in such areas is likely a topological surface gap resulting from strong spin fluctuations [98, 229] in regions with sufficiently uniform alignment of magnetic moments, while ungapped areas may have increased defect density which leads to non-uniform magnetic fields. [250] Previously reported gaps, both calculated [47, 98, 228, 258, 259] and experimentally observed [42, 223, 228–230, 247, 250], are within a range from 15 meV to 225 meV. Unlike in the spectroscopy of gapless regions presented in this chapter and also unlike the aforementioned ARPES reports, where the gap was shifted towards the valence band side, the sample is observed to be nearly undoped in gapped regions.

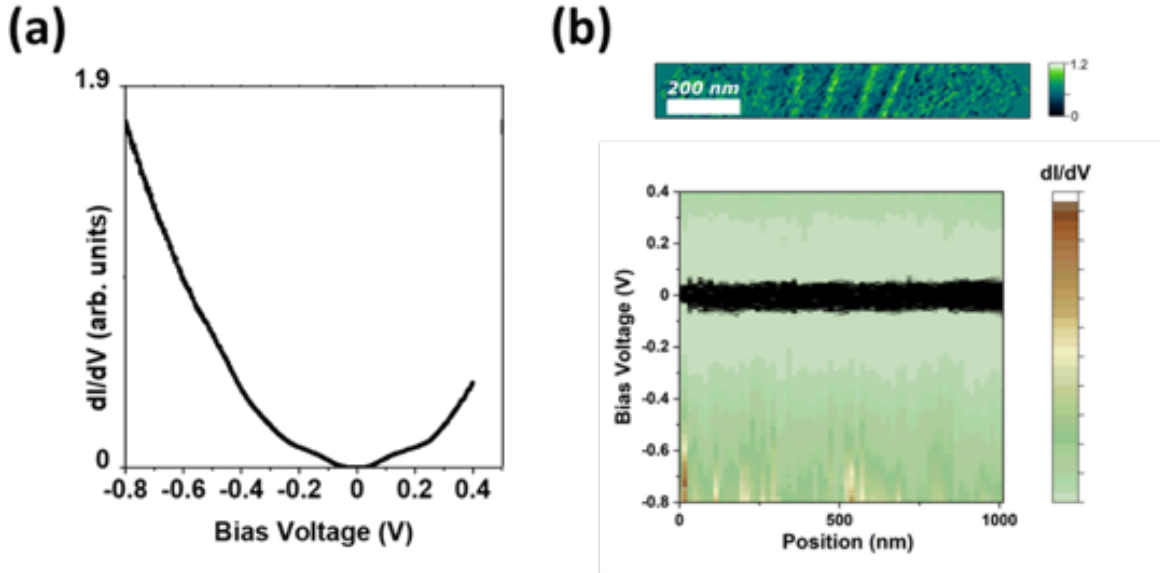


Figure 6.5: (a) Scanning tunneling spectra averaged over a line of one micron, with a uniform band gap ($V_B = 500 \text{ mV}$; $I_T = 40 \text{ pA}$). (b) Top: topographic image along which the line spectrum was obtained. Bottom: conductance map along the line corresponding to the spectroscopy from (a).

Within gapped regions of the crystal, there is little fluctuation of the size or position of the gap even across large areas of 1 μm or more (See Figure 6.5). The fluctuation in gap size from area to area might be due to unavoidable intrinsic non-uniform magnetic field. Theoretical calculations have suggested that the anti-parallel alignment of MnBi moments with respect to the Mn layer may lead to a reduction in the Dirac point gap size.[250]

6.3 Topological phases in edge states of MnBi_2Te_4

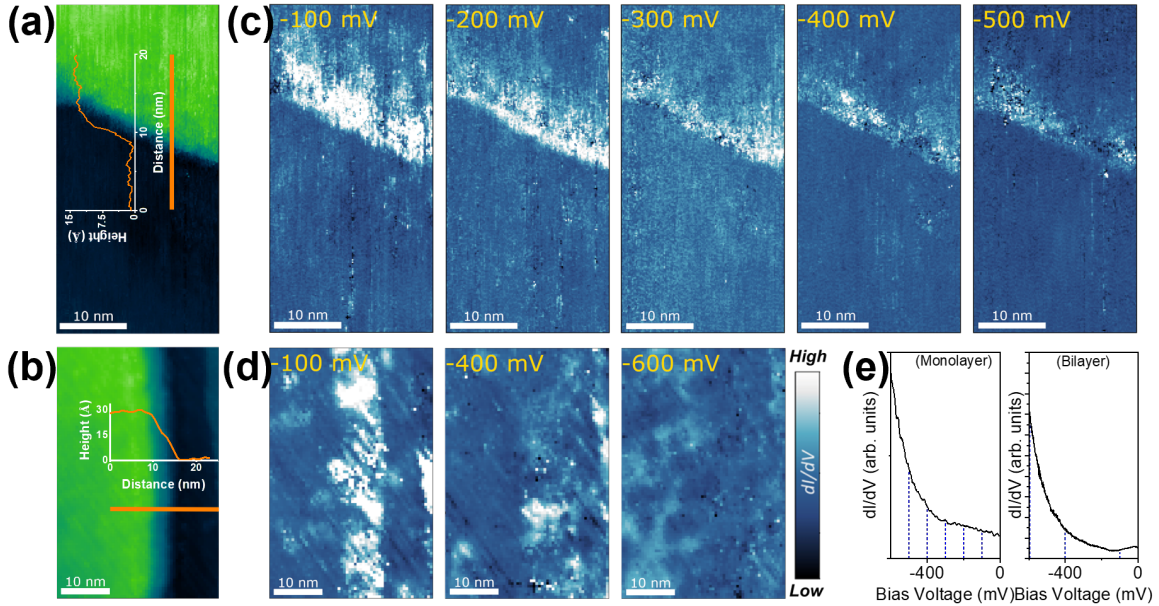


Figure 6.6: (a, b) Topographic scans of (a) monolayer ($V_B = 1000$ mV; $I_T = 350$ pA) and (b) bilayer ($V_B = 1000$ mV; $I_T = 200$ pA) step edges of MnBi_2Te_4 . (c, d) dI/dV maps ($I_T = 200$ pA) of the (c) monolayer and (d) bilayer step edges taken across a range of bias voltages as indicated in each panel. (e) Scanning tunneling spectra from the same area as the (left) monolayer and (right) bilayer step edges.

Prior theoretical predictions and some experimental results have claimed that MnBi_2Te_4 presents thickness dependent topological phases such as QAH at even-numbered layer edges, and axionic phases at odd-numbered edges. [232–234] In order to find signals of such phases, the electronic properties at edges of different thicknesses are characterized via dI/dV maps

acquired at $T=10$ K. In Figure 6.6, topography and dI/dV maps taken across a range of bias voltages on odd-numbered (monolayer, ~ 1.38 nm) and even-numbered (bilayer, ~ 2.84 nm) step edges are shown. Edge states emerge at the monolayer edge at energies associated with the surface states, suggesting the existence of the proposed QAH phase, and this signal fades away as the energy is increased further into the valence band. The width of these edge states extends approximately (5 ± 1) nm across the top of the monolayer edge. The signal over the rest of the surface is low (on the order of pA) for the energy range from -300 meV to the Fermi level, as revealed by spectroscopy taken from the same areas (Figure 6.6(e)), indicating the surface is nearly gapped away from these edges. Since uncompensated Mn-layers should break the time reversal symmetry over the surface, edge states across odd-number steps such as this one are suggestive of QAH phase. These results agree with previously seen edge states at odd layer numbered thin MnBi_2Te_4 samples[234].

Topography on the bilayer edge along with corresponding dI/dV maps again revealed the presence of edge states. As in the monolayer edge, the dI/dV signal at -100 meV is highest along the edge and fades away as we approach energies associated with the bulk bands. In the spectroscopy at the surface (Figure 6.6(e)) gapless surface states were measured, yet spectroscopy from an area near the bilayer edge reveals a considerably lower density of states at energies between -200 meV and the Fermi level, just as for the monolayer edge. Gapped spectroscopy on an even layer numbered edge would indicate the presence of a strong magnetic field, which may originate in an antiferromagnetic to ferromagnetic transition[260], or would come as a signature of the predicted axion insulator phase. A more likely possibility is that the edge states here are trivial, created by local defects. This latter case is supported by the instability of the edge state observed in the bilayer as compared to the monolayer edges.

6.4 Conclusion

In this chapter, we studied the variation of spectroscopic features seen in separate regions of the same MnBi_2Te_4 crystals, where a finite density of states inside the band gap indicated the existence of topological surface states. The small magnetic fluctuations at the surface, due to surface defects or local variations such as temperature, are not generally sufficient to disturb the robust surface states in MnBi_2Te_4 . In some rare cases, uniform gapped spectroscopy across micron-sized surfaces indicates the existence of strong magnetic fields which break the time reversal symmetry. In such surfaces where the condition for topologically protected surface states is broken, the edge states measured at monolayer or odd-numbered step edges contributes evidence for the presence of QAH phase. Surprisingly, in the case of bilayer or even-numbered step edges, the emergence of similar edge states is seen. Two possibilities arise as likely explanations: (1) presence of strong intrinsic magnetic field forcing a transition from antiferromagnetic to ferromagnetic phase, or (2) existence of trivial scattering centres at even edges that induce the local states at the edge, which could signify the presence of an axionic phase in the same sample, though at different edges.

These data help to elucidate the discussion surrounding the presence of gapped states in MnBi_2Te_4 and provides valuable insight that is necessary for exploring the manifestations of topological structure in materials with spontaneously broken time-reversal symmetry. Further investigation is required to understand the nature of the local electronic behaviour at the edge states in this material. MnBi_2Te_4 could be incorporated into vertical heterostructures, leveraging its unique combination of properties by tuning the local electronic or magnetic structure via spintronics, for example by using the twist angle between MnBi_2Te_4 layers to control alignment of the interlayer magnetic fields.

Chapter 7

Outlook

In this work, scanning tunneling microscopy and spectroscopy were used to examine features which modulate the band structure of TMDs. In semiconducting TMDs, the band structure modulation induced by defects was characterized. A fabrication technique for assembling high quality van der Waals heterostructures was described, and with this technique a device was made consisting of two crystals of dissimilar lattice symmetry. Finally, a band gap in the topologically protected surface states of MnBi_2Te_4 , opened by its intrinsic magnetic field, was observed via scanning tunneling spectroscopy. Through these interconnected experiments, valuable insights can be gained regarding the optimization of devices crafted from 2D materials, and how to tailor those devices for optimal performance in conjunction with scanning probe techniques.

In Chapter 3, we describe the “inverted” dry transfer method, which facilitates the assembly of atomically clean van der Waals heterostructures. While there existed methods to clean transfer polymers off the final surfaces of 2D devices, they often left interfacial bubbles and wrinkles that impacted device performance[261]. The first fully dry techniques[262], which exploited the differences in thermal expansion coefficients of polymers and 2D materials to mechanically peel off the transfer polymer, still did not achieve samples that were reliably clean enough for surface studies. A technique described in [2], which can be considered the first of this genre of inverted transfer techniques, achieves polymer-free interfaces and sur-

faces. The work in Chapter 3 of this thesis adapted this technique, adding some steps which benefit overall yield and improved sample outcomes.

In Chapter 4, insight into the electronic structure of semiconducting TMDs ReS_2 and WSe_2 is obtained by characterizing the defects at their surfaces via STM/S. The defect densities at the surface were quantified, and in ReS_2 , analysis of the spectroscopic signatures allowed identification of the most common type of defect as oxygen adsorbed at vacancy sites. This fundamental characterization of their lattice structures, electronic structure, and of the nature of the defects in these materials, helps inform future experiments which seek to incorporate or engineer these properties.

Accordingly, in Chapter 5, following the inverted dry transfer protocol described in Chapter 3, an ReS_2 /graphene device was made and used to study moiré patterns in a heterostructure with mismatched lattice symmetries. The mismatched symmetries were reflected in the emerging moiré pattern, a series of one-dimensional stripes with periodicity ~ 5.2 nm. As the semiconducting crystals used in these studies have reduced conductivity at low temperature which inhibits scanning tunneling probe experiments, these experiments were carried out at room temperature. As such, spectroscopic results were limited, but it was possible nonetheless to observe band alignment and some features in the graphene spectrum which were attributed to scattering from the presence of defects in the TMD.

In Chapter 6, characterization of the spatial homogeneity of the electronic structure of the antiferromagnetic topological insulator MnBi_2Te_4 provided much needed information towards its use as an element of devices incorporating exotic phenomena which arise from its topological order. More recent works have only just begun to delve into the potential of 2D devices which incorporate topological systems[263–267].

Altogether, this thesis details the characterization and fabrication of 2D van der Waals heterostructures specially designed for scanning probe techniques. Despite the promise shown

here for achieving such atomically clean heterostructures, there still exist many challenges. Beyond this work, the inverted dry transfer fabrication method could be expanded upon to further adapt and build on the recipe. The current status of the inverted dry transfer method still leaves some polymer at the interface between the bottom of the device and the substrate. Since 2D materials are so sensitive to the dielectric environment influencing the surface[268], the uniformity and cleanliness of the surface below the device may be just as important as the one above. Thus, it may be desirable to incorporate elements of other recipes which either decouple the device from the substrate, such as the use of hBN as a substrate[269], or which might prevent the contamination of the bottom-layer of the device, like the use of gold as a transfer layer[270]. Furthermore, contact engineering could help overcome an issue that is pervasive in 2D devices, since the performance of 2D semiconductors is often limited by the choice of contacts[271, 272]. Above all, this thesis represents a small part in the explorations into moiré material engineering, whereby incorporating novel 2D materials into devices opens up opportunities for leveraging different symmetries, and improving or introducing entirely new characteristics.

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Chapter 8

Appendices

8.1 Tunneling Current Derivation

Before obtaining the reflection and transmission coefficients, we can make an assumption that particles are incident from $z < 0$, with an incident amplitude of A and a reflected amplitude of B . This simplifies the transmitted wave (in $z > a$) since there is nothing in $z > a$ to reflect particles. We can take $D = 0$ and simplify to:

$$\psi(z) = \begin{cases} Ae^{ikz} + Be^{-ikz}, & \text{if } z < 0. \\ Ce^{ikz}, & \text{if } z > a. \end{cases} \quad (8.1)$$

Now we can calculate $j(z, t)$, the probability current density.

$$j(z, t) = \frac{\hbar}{2mi} \left[\psi^\dagger(z, t) \delta_z(\psi(z, t)) - \psi(z, t) \delta_z(\psi^\dagger(z, t)) \right] \quad (8.2)$$

$$j(z, t) = \begin{cases} \frac{\hbar k}{m} (|A|^2 - |B|^2), & \text{if } z < 0. \\ \frac{\hbar k}{m} |C|^2, & \text{if } z > a. \end{cases} \quad (8.3)$$

From this, two cases emerge: $E > V_0$ and $E < V_0$, where V_0 is the barrier height. The solution which is relevant to STM is $E < V_0$, as electrons in the sample and tip will have less energy than the potential barrier between these two regions. As such, the transmission

coefficient that we find from this case will be equivalent to the tunneling current with a voltage applied.

With that in mind, we can define the reflection (R) and transmission (T) coefficients, given by the ratio of the reflected wave or the transmitted wave to the incident wave, respectively:

$$R = \frac{|B|^2}{|A|^2} \quad \text{and} \quad T = \frac{|C|^2}{|A|^2} \quad (8.4)$$

and we can also define $K = \frac{1}{\hbar}(2m(V_0 - E))^{\frac{1}{2}}$ for $E < V_0$. The solution for Schrödinger's equation inside the potential is:

$$\psi(z) = Fe^{Kz} + Ge^{-Kz}, \quad 0 < z < a \quad (8.5)$$

Now that we have a solution both inside and outside the potential, we can relate them by requiring that both $\psi(z)$ and $\delta_z\psi(z)$ are continuous at $x = 0$ and $x = a$. This gives a system of equations:

$$\begin{aligned} A + B &= F + G \\ ik(A - B) &= K(F - G) \quad \text{at } z = 0, \\ Ce^{ika} &= Fe^{Ka} + Ge^{-Ka} \\ ikCe^{ika} &= K(Fe^{Ka} - Ge^{-Ka}) \quad \text{at } z = a \end{aligned} \quad (8.6)$$

Which can be solved to get R and T .

$$R = \left[1 + \frac{4E(V_0 - E)}{(V_0)^2 \sinh^2(Ka)} \right]^{-1} \quad (8.7)$$

$$T = \left[1 + \frac{(V_0)^2 \sinh^2(Ka)}{4E(V_0 - E)} \right]^{-1}$$

We see that T approaches zero in the limit of E going to zero and that it scales monotonically with E . In fact, if $Ka \gg 1$, then $\sinh(Ka) \approx \frac{1}{2}e^{Ka}$, and we can substitute this into T in equation 8.7:

$$T = \frac{1}{1 + \frac{V_0^2}{16E(V_0 - E)} e^{2Ka}} = \frac{\left[\frac{16E(V_0 - E)}{V_0^2 e^{2Ka}} \right]}{\left[\frac{16E(V_0 - E)}{V_0^2 e^{2Ka}} \right] + 1} \quad (8.8)$$

Considering that the portion in the square brackets is very small, the denominator can be approximated as equal to 1. Thus:

$$T \approx \frac{16E(V_0 - E)}{V_0^2} e^{-2Ka} \quad (8.9)$$

which corresponds to the amount of current which is transmitted, that is, the tunneling current we measure in STM:

$$I_t \propto e^{-2Ka} \quad (8.10)$$

8.2 STM Tip Fabrication and Characterization

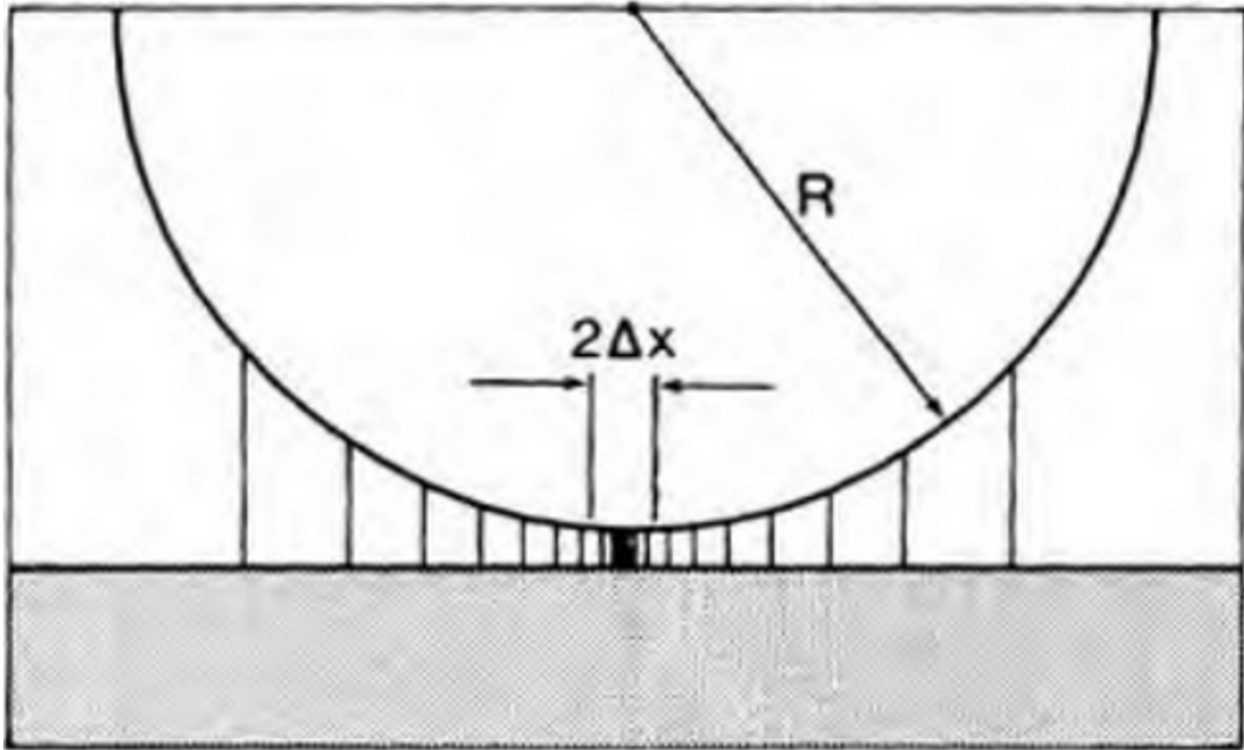


Figure 8.1: Estimation of the lateral resolution in STM. The tip apex, with radius R , is very close to the sample surface. The tunneling current is concentrated in a small region around the origin, $x = 0$. With $R = 100$ nm, the radius of the tunneling current column is approximately $\Delta x = 4.5$ nm.[110]

In order to obtain high resolution images in STM, it is crucial for the radius of the tip at the apex to be as narrow as possible (Figure 8.1). In order to resolve individual atoms, it is therefore essential to achieve the smallest value for R possible. Tips with radius below 100nm can be achieved regularly and will give good resolution, but the sharpest tips have radius below 20nm (Figure 8.2b). Two principal methods exist for the fabrication of tips: the pull-and-cut technique and the chemical etching technique.

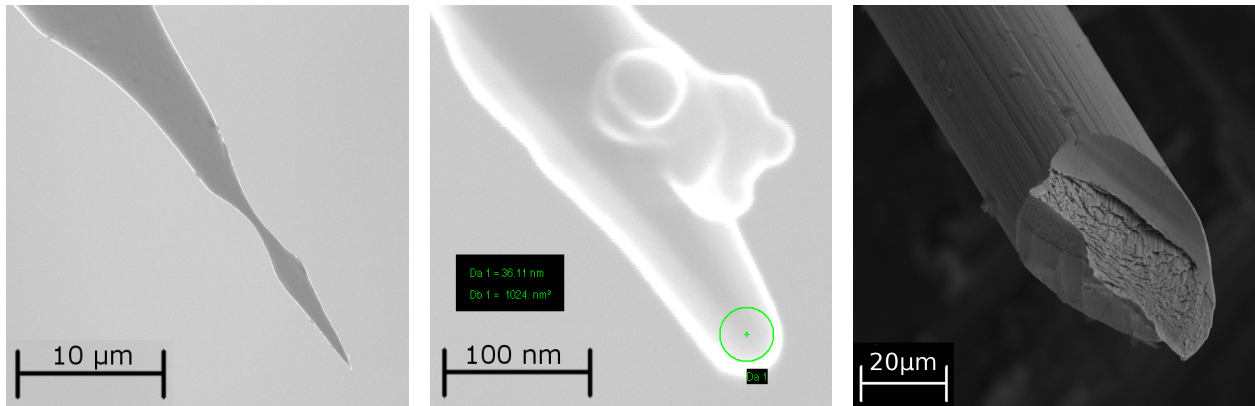


Figure 8.2: STM tips imaged by scanning electron microscope. Working distance: 5.7 mm. (a) Etched W tip. (b) Higher magnification view of (a), with measured radius of curvature 18 nm. (c) Mechanically cut qPlus AFM/STM W tip.

The pull-and-cut technique is primarily used for Pt/Ir tips. Here, wire cutters are used to grip the end of the wire. The other end is held with tweezers and the wire cutters are pulled away while cutting. SEM images of such tips reveal a rough structure macroscopically, but with only a small radius at the apex nonetheless (Figure 8.2c). Since the tunneling current is exponential, only these atoms at the tip apex contribute. Therefore this method is suitable, so long as the apex ends up with the correct shape.

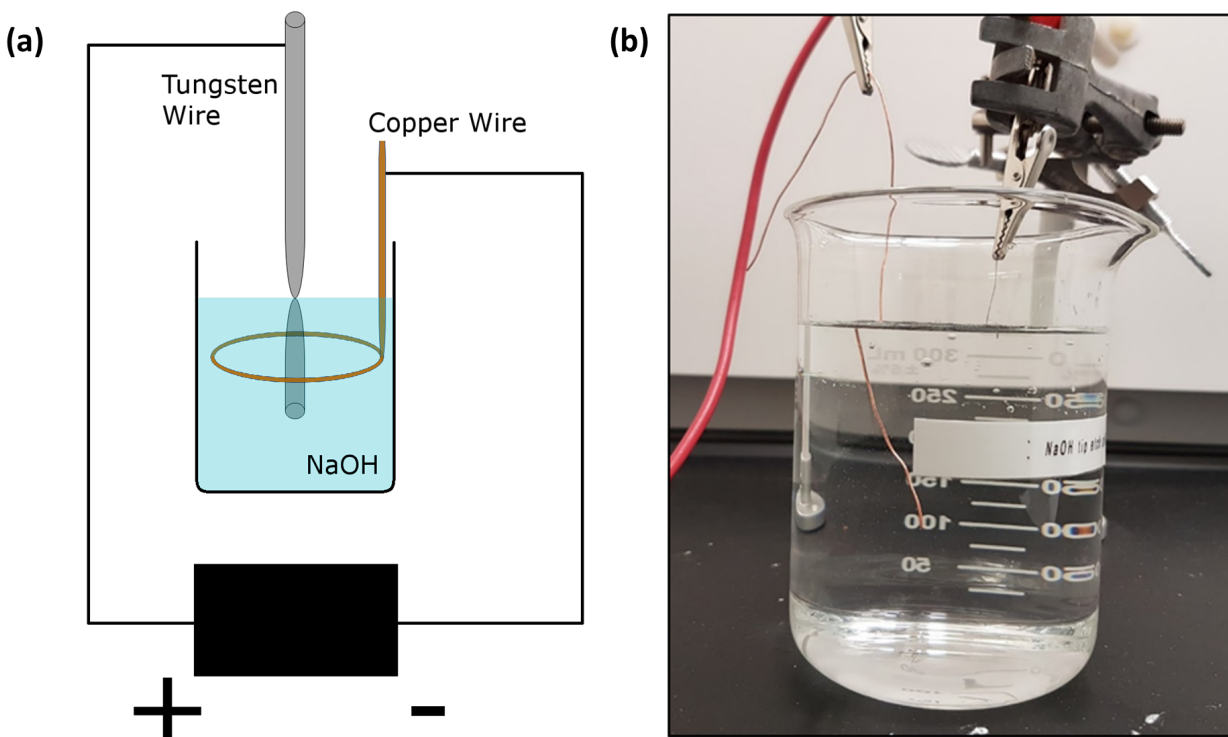
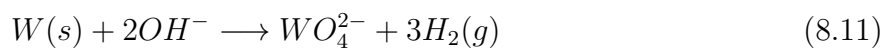


Figure 8.3: Tip etching setup. (a) Schematic. The black box represents the power supply which controls the current and voltage during etching. (b) Experimental setup.

For tungsten (W) tips, an etching setup was constructed (Figure 8.3). This setup is designed to prepare tungsten tips through a one-step electrochemical etching process. Tungsten wire (0.25 mm diameter) is etched at the interface of a NaOH solution in air through a one step electrochemical reaction,



This reaction is utilized to shape the wire into a sharp, conical tip. Tips with sharpness as low as 18 nm have been obtained using this method, as seen in the SEM images in Figure 8.2. To achieve this, a circuit was constructed (Figure 8.3), in which the tungsten wire acts as an anode and a copper wire as a cathode.

Both wires are attached to a stand and one end of each wire is submerged in a solution of 2M NaOH (24g in 300mL distilled water). The copper wire should be well immersed in the solution in a ring geometry. This shape ensures the etching on the tungsten wire is symmetric. The setup should be free of vibration to prevent breaking the meniscus during etching – else the wire will need to be resubmerged, and other undesirable macroscopic features can appear, such as the narrow section seen in Figure 8.2a).

The tungsten wire need only be submerged about 0.5 cm. The length determines the weight of the submerged portion – when the wire is too thin at the meniscus of the solution to support this weight, the submerged portion will detach. A smaller submerged portion increases the time for the reaction and improves the final tip radius that can be achieved.

The other ends of the wires are connected with alligator clips to a power supply (Keithley 2231A-30-3 DC). A voltage of 9 V and a current of approximately 18 mA results in a reaction time of approximately 15 minutes. The end of the reaction is determined by a sudden drop of the current to zero, associated with the submerged W portion detaching. The wire is removed from the solution when the current is interrupted. Afterwards, the NaOH solution is cleaned off with isopropanol (IPA) and distilled water.

Commercial W tips have been used in addition to tips fabricated in the lab, and comparison with SEM has shown the tip radius to be similar to those produced by the method described here.

8.3 General Preparation of Samples for STM

If the tunneling occurs through a non-metallic atom on the tip, the measured signal will not represent the true electronic structure of the surface[115]. Consequently, with the goal of characterizing a surface, sample preparation techniques which minimize the presence of contaminants are essential. But more than this, the surface should remain atomically clean for

the duration of the experiment. Therefore, preparation of samples for STM follows procedures designed to minimize the amount of outgassing materials introduced to the system, while ensuring good electrical contact and surface condition is maintained. This section describes techniques for generic preparation of samples before they are introduced to UHV in the system.

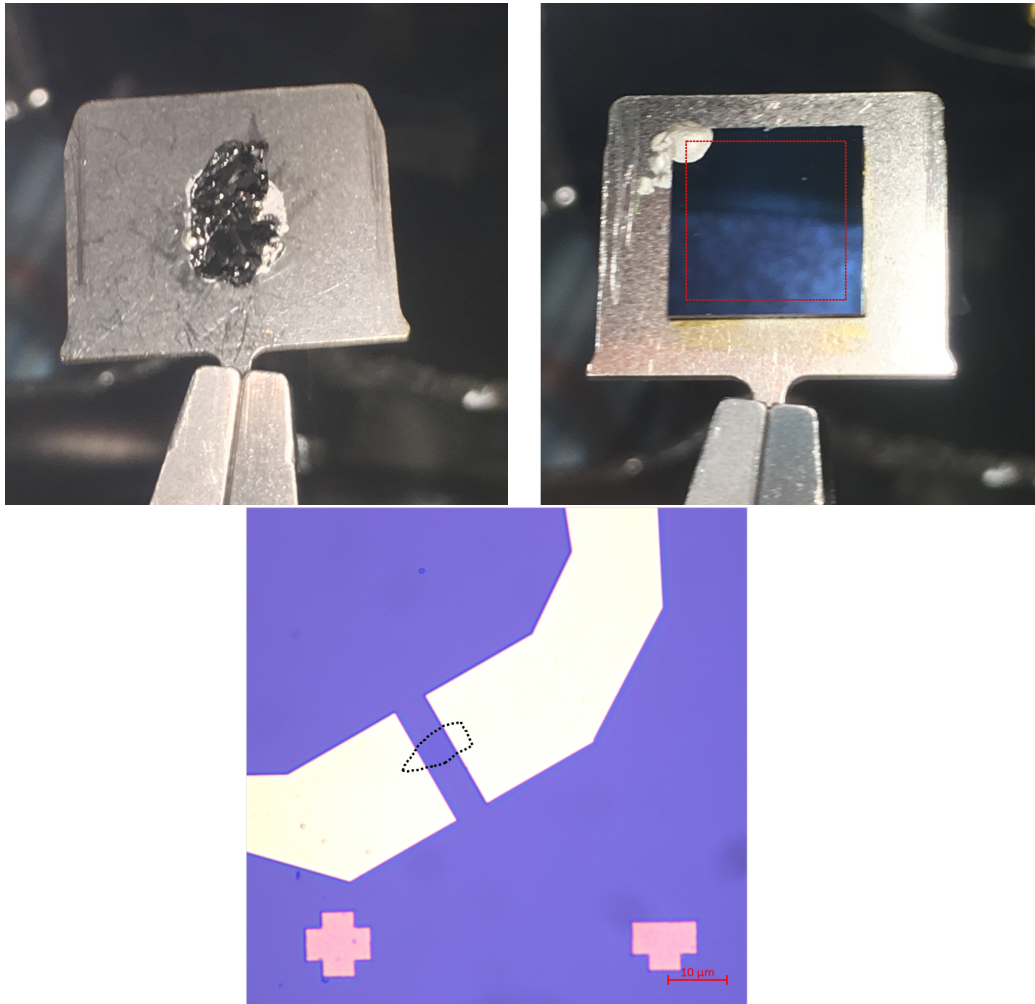


Figure 8.4: Preparation of samples for STM. (a) Natural graphite crystal on STM sample plate. (b) Chemical vapour deposition (CVD) graphene (red outline) on silicon wafer glued to sample plate. (c) Monolayer graphene (black outline) on an SiO₂ substrate, connected with gold contacts.

The Si/SiO₂ substrates used for these experiments are insulators. If the sample covers

the entire substrate evenly (e.g. graphene grown with chemical vapour deposition) epoxy can be used to secure the substrate. Then, a small amount of epoxy can be applied on the corner of the sample down to the sample plate. The epoxy then electrically connects the sample to the plate.

In the case where samples are prepared through mechanical exfoliation, the area of a crystal flake is on the order of $10 \mu\text{m}^2$. To achieve this size and to make contact with the STM plate, we begin with a clean silicon substrate (Si/SiO₂ with 285nm native oxide) and use standard e-beam lithography with poly(methyl methacrylate) (PMMA) as a resist to pattern contacts onto the device. First, a grid of small features is created on the surface. The regular sample fabrication methods are used to get the desired sample onto the substrate (Figure 8.4c). Using the grid for alignment, contacts can be precisely placed just on the edges of the sample, leading off to larger metal pads far from the sample. Using a wire bonder these larger pads allow the sample to be integrated in devices, or simply connected to an STM sample plate (Figure 8.4c). This process inherently contaminates the surface with resist, which can be cleaned with further annealing and AFM brooming steps as described in Chapter 3. To avoid these additional cleaning steps in samples which do not require a back gate, it is often more convenient to simply metallize the entire substrate (e.g. with 5nm Ti/50nm Au), as samples placed on the substrate will be guaranteed to have electrical contact to the sample holders.

8.3.1 Quasi-*in-situ* sample cleaving

The experiments described in Chapters 4 and 6 are on bulk crystals. Rather than exfoliating crystals onto a substrate, bulk crystals are glued directly to STM sample plates with conductive silver epoxy (Epo-Tek H21D). In order to alleviate the impacts of the environment, bulk crystals are cleaved (by removing the top surface with adhesive tape) just before introducing the sample to the load-lock. This process reduces the time the exposed surface of the sample spends in air to less than 1 minute. For more reactive samples, this amount of time may be still too long, and a way to exfoliate the sample *in-situ* is required. Thus, when studying bulk crystals which are less stable in air, it is important to find a method to introduce the sample into the UHV environment of the STM without exposing them to any degradation whatsoever. One method is to glue a small metal screw onto the bulk crystal, and to knock the screw off within the UHV chamber. Another way is to cleave samples in a glove box under inert atmosphere, then spin coat a protective layer onto the surface and remove it once the sample is introduced to UHV. An example of a crystal which is affected quickly is black phosphorus, which is completely degraded within a matter of hours[273]. For some crystals, the effects are more subtle, while for others the rate of degradation is completely unknown.

Techniques for in-situ cleaving require specific capabilities which may not exist in all UHV systems. A simple technique to prepare bulk crystals “quasi-*in-situ*” is thus described, which is possible in any system with a gas purged load-lock chamber.

1. First, attach the bulk crystal to a stainless steel STM sample plate (e.g. with conductive epoxy, Epo-tek H21D).
2. Apply a long piece of semiconductor grade adhesive tape over the crystal, and press it firmly. To ensure the cleanest sample possible, cut the tape to just the size required to cover the entire bulk crystal, plus about 1-2 cm.

3. Fold the tape over so that the crystal remains covered, but the rest of the tape sticks out perpendicular to the sample plate.
4. Load this sample plate into the load-lock of the chamber.
5. Apply a positive pressure ($> 1 \text{ atm} = 15 \text{ PSI}$) of high purity nitrogen gas (99.9993%) through the load-lock's purge system.
6. Using long forceps, quickly tear the tape from the crystal in order to cleave the top surface.
7. Shut the load-lock, start the pumps, and stop the flow of gas.

The time the sample surface spends “exposed” depends on two factors: how long it takes to shut the load-lock, and how long the pumps require to get the load-lock to high vacuum pressures. Thus, it is helpful to have a fast-entry access door on the load-lock to facilitate this process, otherwise having a blank flange with its gasket ready one can tighten the minimal number of bolts necessary to start the pumps. Despite these two limitations, the “exposed” time spent in air is effectively zero, since the positive nitrogen pressure ensures a clean environment from the moment the sample is cleaved.

8.4 STM Calibration

In this section, STM results on natural graphite samples (Graphit.de), prepared using the method described in 8.3, are presented. These images are used to calibrate the piezos which control the tip motion during scanning. For the STM images to be scaled properly, each piezo must move by the same amount for the same applied voltage. These piezos will expand when an electric field is applied, and the relationship between the expansion and the applied voltage is constant. By determining this constant factor, each piezo can be adjusted to have the same proportionality between applied voltage and expansion.

In order to set the correct constant factor for each piezo, one has to measure a known structure with atomic resolution. The well-known values for the lattice parameters of graphite, its distinct band structure and simple elemental composition make it a typical candidate for calibration. The following section describes calibration of the STM with graphite samples.

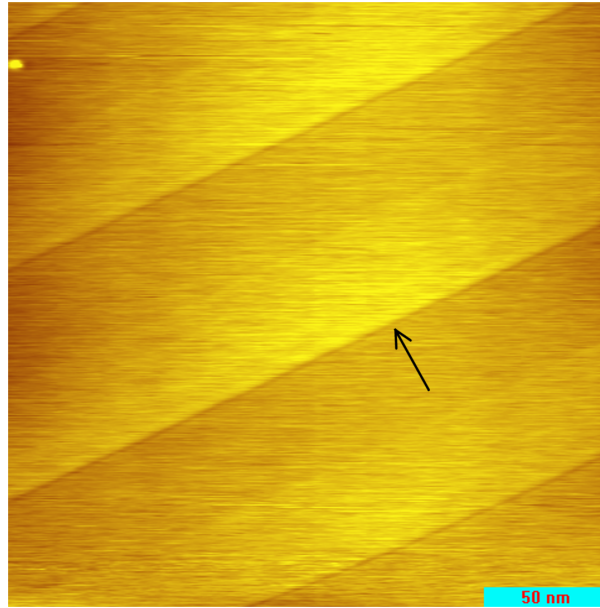


Figure 8.5: STM of graphite step edges. $V_b=0.1V$; $I_t=500pA$. Size=250nm.

Topography. The procedure for imaging bulk 2D crystals begins with imaging larger areas (on the order of a few hundred nanometres). In doing so, we can find step edges on the surface, as seen in Figure 8.5. Finding these steps is the initial stage in attempting to resolve the surface, as it helps to confirm the sample is relatively free of contamination. Once the step edges are located, the lattice is imaged by moving onto the terraces and reducing the scan size gradually. Graphite is better resolved with a low bias voltage ($V_b=100mV$) and a high tunneling current ($I_t=500 pA$). By imaging the same area for several hours, drift is minimized and a more accurate calibration can be made. When acquiring scans at intermediate temperatures, even more care must be taken to ensure the heater's PID controller has achieved a steady state before taking measurements.

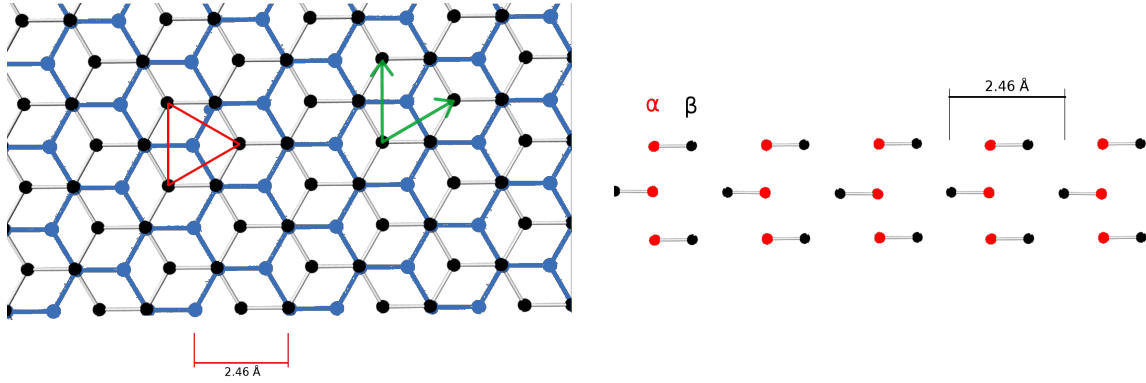


Figure 8.6: Graphite lattice schematic in A-B-A stacking. Left: Top-down view of two layers. Red triangle represents the observed topography in STM. Right: Side-view. The length of one period ($2.46 \text{ \AA}$) used in the calibration measurements is indicated, and the A and B vectors are drawn as green arrows.

Consider for example Figure 8.6, which shows a schematic of the atomic lattice of graphite. The atomic layers of graphite consist of a hexagonal lattice in $A - B - A$ stacking, meaning the atoms of the second layer are offset from the first by one unit cell distance. Half the atoms in a hexagon will be aligned above a carbon atom in the next layer (α atoms), and half will be above an empty space (β atoms).

Due to the stacking between layers, two dissimilar sets of three carbon atoms exist. This inequivalence is reflected in the electronic structure, as observed by the STM (Figure 8.7), where only half the atoms in the surface layer are observed. Instead of a hexagonal lattice, a triangular lattice showing every other atom is seen (for a total of 3 per hexagon)[274–278]. It was suggested that the β atoms have a greater contribution to the tunneling current at low bias, but it is possible to switch between α and β sites by alternating the bias polarity[274]. In graphene, where such stacking is not present, the hexagonal lattice is observed once more[279].

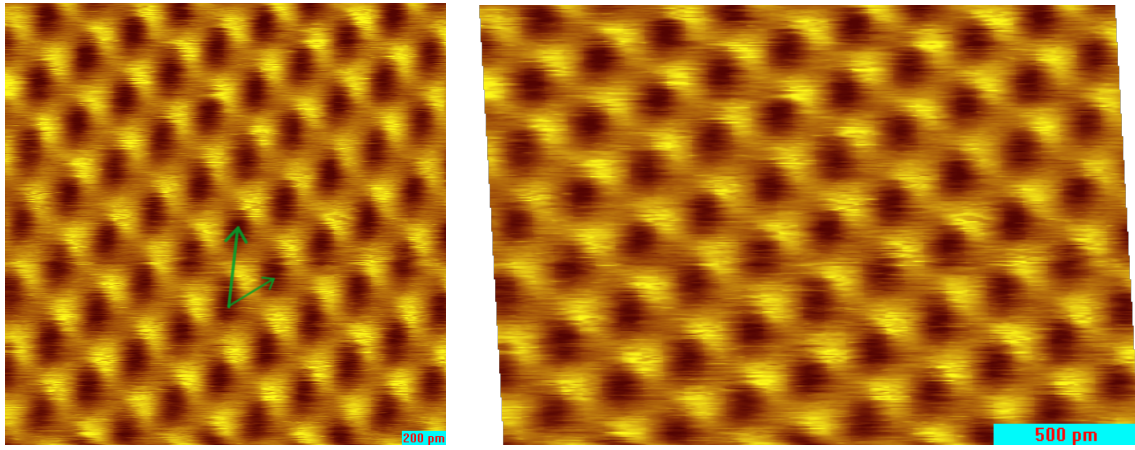


Figure 8.7: Atomic resolution of graphite. $V_b=0.1\text{V}$; $I_t=500\text{pA}$. Size=2nm. Taken with RHK STM. Left: Raw image before calibration, green arrows indicate the A and B vectors. Right: Final recalibrated image.

Calibration of the STM is done by first obtaining the atomic lattice of graphite, as in Figure 8.7a. The lattice is well resolved and the expected triangular contrast is suitable for calibration. Since the lattice constants of graphite should both be equal ($a = b = 0.142\text{ nm}$), we can compare the values we get for each with the expected values to determine all the necessary scaling parameters. These parameters describe a stretch in the x - and y -axis to correct the magnitudes of the vectors, as well as a skew factor to correct the angle between them. These constants describe the correction on the piezos.

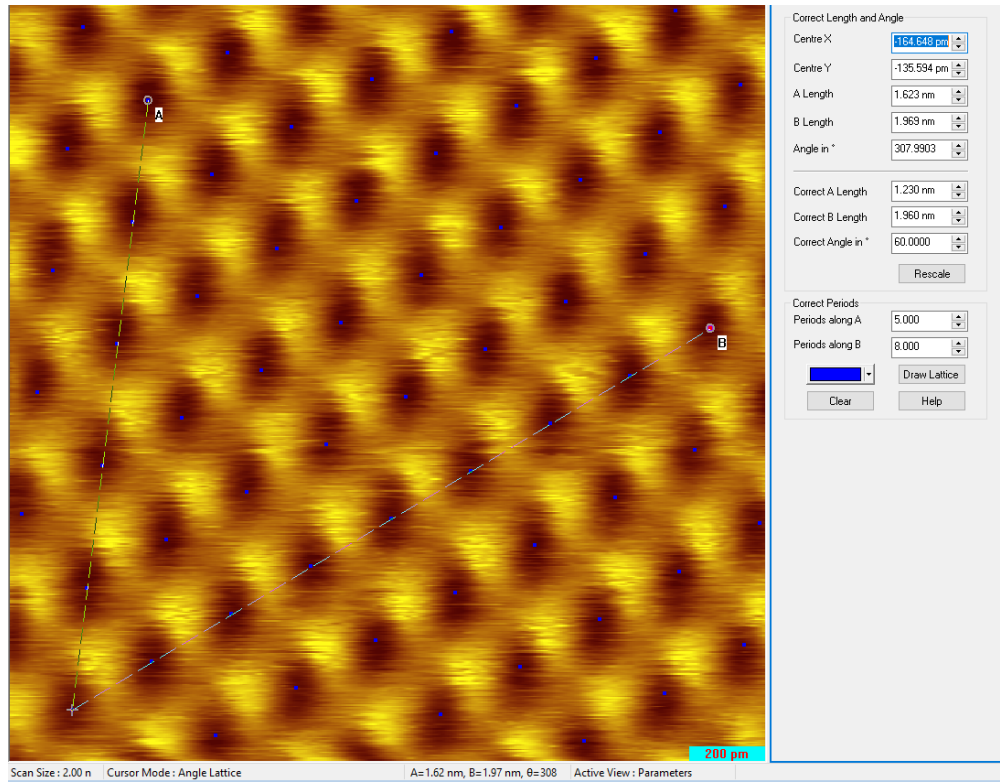


Figure 8.8: Calibration software used to measure and project the lattice.

Calibration on the RHK system will be explained based on Figure 8.7a. The “A” and “B” vectors are drawn manually on the image (green arrows in Figure 8.6a and 8.7a), and the number of periods along these vectors is counted. For these measurements, a period is defined to be across the centre of adjacent hexagons (0.246 nm), so that measurements are made from the dark spots in the images.

By inputting the correct values for the lattice parameters, we can calculate the factors for x , y , and the skew. For this particular image, these are $x = 1.098$, $y = 0.758$, $skew = -3.2^\circ$, and the result is Figure 8.7b. While the borders of the image are no longer square due to the skew applied, the hexagonal lattice is now perfectly symmetric, representing the true lattice of the crystal. Scans taken after this recalibration will be prescaled by the STM to have square image frames. In practice, the calculation of the correction factors is performed automatically using the STM’s software. If instead we want to manually calculate the correction factors,

we must first determine the lattice vectors on our image. The measured values for the a and b vectors on the image are 2×1 matrices, separated by an angle ϕ :

$$\vec{a} = \begin{pmatrix} a_x \\ a_y \end{pmatrix}, \quad \vec{b} = \begin{pmatrix} b_x \\ b_y \end{pmatrix}, \quad \phi = \cos^{-1} \left(\frac{\vec{a} \cdot \vec{b}}{|\vec{a}| |\vec{b}|} \right) \quad (8.12)$$

We will apply a 2×2 affine transformation matrix $\mathbf{A}$ to the vectors to find the correction factors. This matrix is a combination of two 2×2 matrices. The right-most matrix is applied first, and applies a skew to correct the angle between the vectors. The left-most of these is a matrix which applies scaling to the vectors by a constant, c_x for the x -components and c_y for y -components:

$$\mathbf{A} = \begin{bmatrix} c_x & 0 \\ 0 & c_y \end{bmatrix} \begin{bmatrix} 1 & \tan(90 - \phi - \gamma) \\ 0 & 1 \end{bmatrix} \quad (8.13)$$

To determine c_x and c_y , we must compare the magnitude of $\vec{a}$ and $\vec{b}$ to the theoretical lattice parameters. To simplify this, we can rotate the image (our axes) such that $\vec{a}$ lies along the x -axis. Then $a_y = 0$ and we can find c_x :

$$c_x = \frac{L}{|\vec{a}|} = \frac{L}{a_x} \quad (8.14)$$

where L is the correct length of the lattice parameters. Before we find c_y , we should apply our skew to the vectors, since the skew matrix will change the magnitude of vectors it is applied to. In principle, one need only apply it along either the x - or y -axis to correct the image. The right matrix in $\mathbf{A}$ applies a shear along the x -axis only – this choice is made such that $\vec{a}$ is unchanged, and we need only determine the skew on $\vec{b}$. This is why c_x was solved for first.

The shearing factor is determined from the angle ϕ between the vectors $\vec{a}$ and $\vec{b}$, and the

correct angle γ . For example in graphite, $\gamma = 60^\circ$. When applied to $\vec{b}$, we get:

$$\begin{bmatrix} 1 & \tan(\phi - \gamma) \\ 0 & 1 \end{bmatrix} \begin{pmatrix} b_x \\ b_y \end{pmatrix} = \begin{pmatrix} b_x + b_y \tan(\phi - \gamma) \\ b_y \end{pmatrix} \quad (8.15)$$

This skewing matrix corrects $\vec{b}$ by changing its x -component. The result can be visualized as a “rotation” towards $\vec{a}$ by an angle $\phi - \gamma$. Since this is explicitly the difference between the measured and the correct angle, the matrix moves $\vec{b}$ to this correct angle γ .

Now we will find c_y , and it should become evident why the symmetry of graphite is necessary for calibration, as we require that the correct lattice parameters have the same magnitude $|\vec{a}| = |\vec{b}| = L$.

$$\begin{aligned} \begin{bmatrix} c_x & 0 \\ 0 & c_y \end{bmatrix} \begin{pmatrix} b_x + b_y \tan(\phi - \gamma) \\ b_y \end{pmatrix} &= \begin{pmatrix} c_x(b_x + b_y \tan(\phi - \gamma)) \\ c_y b_y \end{pmatrix} \\ &= \begin{pmatrix} \frac{L}{a_x}(b_x + b_y \tan(\phi - \gamma)) \\ c_y b_y \end{pmatrix} \end{aligned} \quad (8.16)$$

$$|\vec{b}'| = \sqrt{\left(\frac{L}{a_x}(b_x + b_y \tan(\phi - \gamma))\right)^2 + (c_y b_y)^2}$$

We can compare the magnitudes of $\vec{b}'$ and $\vec{L}$ to solve for c_y :

$$1 = \frac{|\vec{b}'|}{|\vec{L}|} = \frac{\sqrt{\left(\frac{L}{a_x}(b_x + b_y \tan(\phi - \gamma))\right)^2 + (c_y b_y)^2}}{\sqrt{L^2}}$$

$$L = \sqrt{\left(\frac{L}{a_x}(b_x + b_y \tan(\phi - \gamma))\right)^2 + (c_y b_y)^2} \quad (8.17)$$

$$L^2 = \frac{L^2}{a_x^2}(b_x + b_y \tan(\phi - \gamma))^2 + c_y^2 b_y^2$$

$$c_y = \frac{L}{b_y} \left(1 - \frac{(b_x + b_y \tan(\phi - \gamma))^2}{a_x^2}\right)^{\frac{1}{2}}$$

We now have expressions for c_x and c_y , both of which depend on only the measured vectors and the (known) correct lattice parameters. We can give these three values to the STM software to calibrate it, or we can apply this correction manually to images taken after this calibration.

8.5 Other Characterization Methods

Atomic force microscopy (AFM) and scanning electron microscopy (SEM) provided supplementary characterization. AFM is a scanning probe technique, similar to STM, where the contrast is instead obtained from the force between the tip and sample. AFM is used to confirm the thickness of samples and to check for surface contamination through topography and roughness measurements, respectively.

SEM is often compared to optical microscopy, where a focused beam of electrons scan back and forth across the surface. The contrast here comes from electrons scattered off the surface — this can also give topographic information for our samples, but is primarily used

to measure the sharpness of STM and AFM probes.



Figure 8.9: Scanning electron microscopes used for characterization and electron-beam lithography. (a) Gemini 500 SEM. (b) Raith Pioneer.

The Scanning Electron Microscope was used for characterizing the sharpness of STM tips both before and after their use. It was also used for electron-beam lithography (EBL) to pattern features onto substrates. In SEM, images are obtained by focusing a beam of electrons onto the sample and collecting scattered electrons.

The electron beam is emitted by an electron gun, and is focused onto the sample through an electron optics system. This system is used to deflect the beam such that the focal point is on the surface of the sample. The same electron optics system deflects the beam back and forth to raster scan across the surface, forming an image.

The electrons scattered by the sample lose some of their energy through absorption processes. This scattering can be either inelastic, producing secondary electrons reflected with energy lower than in the initial beam, or elastic, which produces high-energy electrons. It is also possible for electromagnetic radiation to be produced. A specific type of detector must be used to measure the energy range associated with returning electrons from each of these processes. The positions and energies of these recaptured electrons are used to reconstruct the topography of the sample.

Images of tips taken by SEM can be seen in Figure 8.2.

The model used for basic metrology of tips was a GeminiSEM 500, seen in Figure 8.9a. The Raith Pioneer was the EBL tool used for patterning substrates. These systems both use standard tungsten tips, and operate under vacuum (below 10^{-9} Torr).

The Atomic Force Microscope is a scanning probe technique similar to STM, but which uses a sharp tip on a cantilever to determine information about the morphology of a surface. The cantilever can oscillate and, depending on the method used, measure different properties from the surface. Rather than obtaining topographic information from the tunneling current, AFM is sensitive to the attractive and repulsive forces between the sample and tip. It therefore lends itself to force measurements, where mechanical or electronic properties like the stiffness or resistivity are obtained. The use of AFM in this thesis was to measure the topology of the samples to determine sample height and roughness. This information is used to infer the number of layers in 2D materials and the cleanliness of the surface.

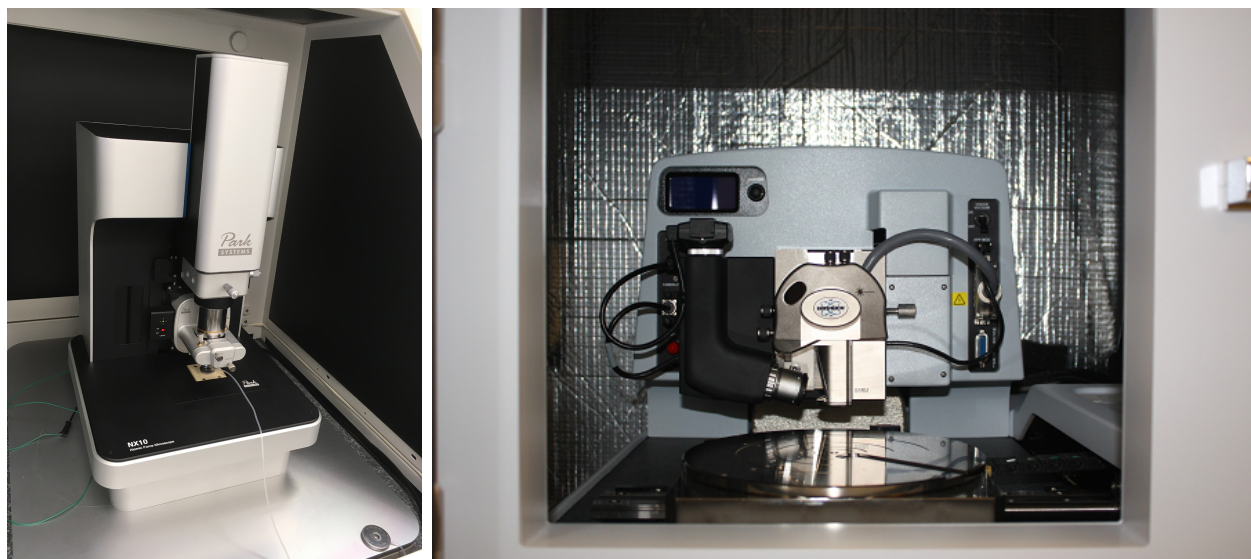


Figure 8.10: Atomic force microscopes. *Left:* Park NX10 AFM. *Right:* Bruker Dimension Icon AFM.

A laser is focused on the end of the reflective tip, and its displacement is measured by a position sensitive photodetector. The tip raster scans across the surface and the frequency of

oscillations (the force measured) changes in reaction to variations in the height of the surface. Similar to STM, a feedback loop keeps the frequency constant, and the amount it must be adjusted to remain at the correct level is used to determine the size of features it scanned over.

In non-contact AFM, images are obtained by oscillating a sharp tip just off its resonance frequency using a piezoelectric motor, around 100 nm above the surface of the sample. Contact and Tapping AFM use similar operating principles, but (as their names suggest) they are either in contact or repeatedly tapping the surface as they move along it. While typically giving greater resolution, the direct contact with samples poses a greater risk of sample destruction or contamination.

As AFM measurements are particularly sensitive, it is crucial to eliminate as much ambient noise as possible. For this reason, both of the AFMs used were contained in isolated acoustic enclosures on vibration-isolating tables.

The particular models of AFMs used for these experiments were the Park NX10 and the Bruker Dimension Icon, seen in Figure 8.10. All images from these tools were obtained in air at room temperature. Data analysis was done using Park Systems' XEI software, as well as Gwyddion and WSxM.

8.6 Closed-Cycle Cryostat Operation

As discussed in the main text, the RHK PanScan Freedom STM used for the bulk of the experiments in this thesis achieves cryogenic temperatures down to 9K through the use of a closed-cycle cryostat (Advanced Research System, Inc.), more commonly used for optical microscopy applications demanding ultra-low vibrations. The procedure for operating the closed-cycle cryostat is crucial to permitting the lowest base temperature possible and to avoid unnecessary maintenance cycles.

The general outline of the cryostat system consist of two closed lines: a water line, and a He line. The water line consist of a series of coils which wrap around the He line, extracting heat in order to condense the gas back to a liquid phase. A reserve tank holds a few liters of filtered water which is filled manually. When filling this tank, water should be added slowly to avoid introducing air bubbles in the water line, which reduce its thermal efficiency. A water pump moves the water through its closed loop around the He lines, and forces it through a radiator and fan unit which forces excess heat out to the room. Helium gas is supplied by a compressed gas tank (99.999%), and the water cooling of the He lines is sufficient to reduce its temperature to nearly 5K at the condenser unit. The condensed He is forced towards the cold head on the STM, where it occupies a small space between the cold finger and the top plate of the STM head. Some loss of temperature occurs here, as the helium exchange gas is inherently less efficient than conduction cooling (as used in more common bath cryostats). However, the absence of any direct contact between the cryostat and the STM chamber prevents almost all vibration from being transmitted to the STM head. To avoid any of the issues mentioned above, there is a specific order in which the cryostat is turned on or off. The procedure for starting the cryostat follows. The procedure for shutting off the cryostat is the same, in reverse order, and without the need to purge the He gas line.

8.6.1 Procedure: Starting the closed-cycle cryostat

1. Check the reserve tank's water supply level and, if needed, refill with filtered tap water up to the fill line.
2. Check the helium "Gas Supply Pressure" on the condenser unit. Ensure it is set to 350 PSI by adjusting the regulator on the compressed He gas tank.
3. Make sure the tip is retracted from the sample. Retracting only 3-5 coarse steps is sufficient, but is close enough to maintain the tip's position on the sample to within

a few hundred nanometers. Lock the STM screw so it makes full contact to the cold plate at the top of the STM head.

4. Change the piezo settings to the low temperature values ($\pm X = 220V$, $\pm Y = 220V$, $Z = 90V$).
5. Turn on the compressor. Check again the “Gas Supply Pressure”. Fine adjustment of the gas line pressure coming from the compressed He tank can be done using the regulator on the cryostat support frame. This value should be set to 1.5 PSI.
6. Purge the He gas line. A pressure relief valve on the cryostat head can be blocked by pressing it in, allowing pressure to build up in the lines. While holding the pressure relief valve shut, close the valve behind it (stopping the supply of He from the tank). A leak valve after the pressure relief valve is then opened briefly, which forces out some of the trapped air in the gas line. The leak valve should be closed, then the pressure relief valve released, then finally the valve from the He supply tank can be reopened. This process can be repeated (typically 3-5 times) until the line is purged.
7. Monitor the gas line pressure as the temperature decreases. As the He condenses, the flow from the fine regulator on the cryostat support frame will need to be adjusted to maintain 1.5 PSI.
8. Once low temperature has been reached, the system should be allowed to thermalize for a few hours to increase stability during measurements.

8.7 UHV System Bakeout Procedure

Through regular use of the STM system, gases, primarily water, enter the system unintentionally whenever samples or tips are introduced via the loadlock. This water adsorbs to the chamber walls, and the vapour pressure it induces can be high enough to limit the system's ultimate pressure. This water gradually desorbs and is pumped away, but at room temperature this process is so slow as to be negligible. In order to accelerate the removal of rest gases, the system undergoes a "bakeout" procedure. During a bakeout, the system is held at elevated temperatures (above 100°C) while the pumps are active. This process requires several days of continuous heating, as the many thermally well-insulated components in the system all must reach a high enough temperature to be fully degassed.

Different approaches exist in how to heat the large STM chamber and its components for the bakeout procedure. Our system includes a bakeout tent, essentially a large insulating box to cover the system. In order to heat the system and its components, a heater fan can be inserted onto the tent, and power strips are permanently affixed at several locations on the exterior of the UHV chambers. However, many non-bakeable elements exist both inside and out of the system, for example sensitive STM samples or electronics which would be damaged by high temperatures. Thus, to ensure successful outcomes for bakeouts and avoid unintentional damage to critical components, the following bakeout procedure was written and describes each step to be performed on our system.

8.7.1 Procedure: Bakeout of the STM system

RHK Panscan Freedom Standard Bakeout Procedure

Ryan Plumadore Benjamin Kollin

Last Reviewed: February 2018

1 Procedure

1.1 System Preparation

1. Ensure system is at low pressure before beginning (below 10^{-5} Torr).
2. Record the planned bakeout time and the initial pressure of the system.
3. Open all gate valves. Refer to Figure 1 for their locations.
 - ☐ Prep. Chamber - SPM isolation valve.
 - ☐ Load lock - SPM valve.
 - ☐ Prep. Chamber - Bypass valve.
4. Disconnect non-bakeable elements (take pictures to record positions). Only two blue cables for the ion gauges should remain connected.
 - ☐ All connectors and cables above table height.
 - ☐ RGA unit, if attached.
 - ☐ Cryo-head unit, including the section with bellows. Clean off the vacuum grease.
5. Manipulator Arm:
 - ☐ If it is not already removed, remove the handle.
 - ☐ Remove motor - rotate to lock pin.

- ☐ Ensure finbar is tightly attached.

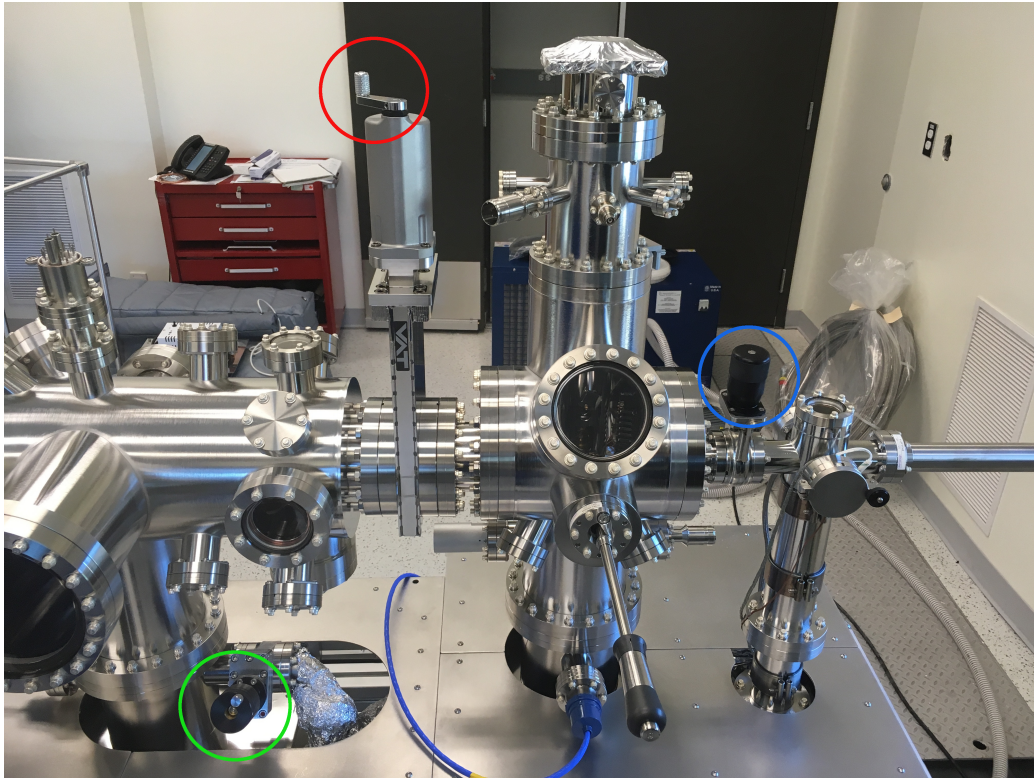


Figure 1: Front view of system. Circled in red is the Prep-SPM valve, blue is the Load lock - SPM valve and green is the Prep-Bypass valve.

6. Attach tent mounting frames (if not already attached).
7. Transfer arm:
 - ☐ Remove handle:
 - Requires a lot of force to pull off.
 - Make sure to catch the small black graphite cube which falls from the bottom of the handle.
 - ☐ Attach the transfer arm plug where the handle was.
8. Cover all openings which will not be covered by the tents with aluminium foil, in particular:

- ☐ The hole around the bottom of the preparation chamber.
 - ☐ The cover plate on the back side of the preparation chamber, where there is a hole cut from the preparation chamber tent - visible in Figure 2.
9. Check that no cables are near any of the heating elements.
10. Clean all surfaces with IPA:
- ☐ Wear gloves and follow all normal safety procedures for IPA.
 - ☐ Using a squirt bottle, spray some IPA on a few kimwipes.
 - ☐ Wipe down all surfaces, including the table surface, viewports, cover plates and edges.
11. Attach tents. The various sections should be fastened together to form a seal around the system.
- (i) SPM. Small hole goes on the wobble stick side.
 - (ii) Wobble stick cover.
 - (iii) Preparation Chamber. Must be slid on around the manipulator arm, **making sure not to touch the bellows**.
 - (iv) Manipulator arm.
 - (v) Transfer arm.
 - (vi) Attach the vent fan to the SPM tent (opposite side from wobble stick).
 - ☐ Slide into slot in the tent to hold securely.
 - ☐ Turn the T-nuts to fasten onto the bracket on the table.

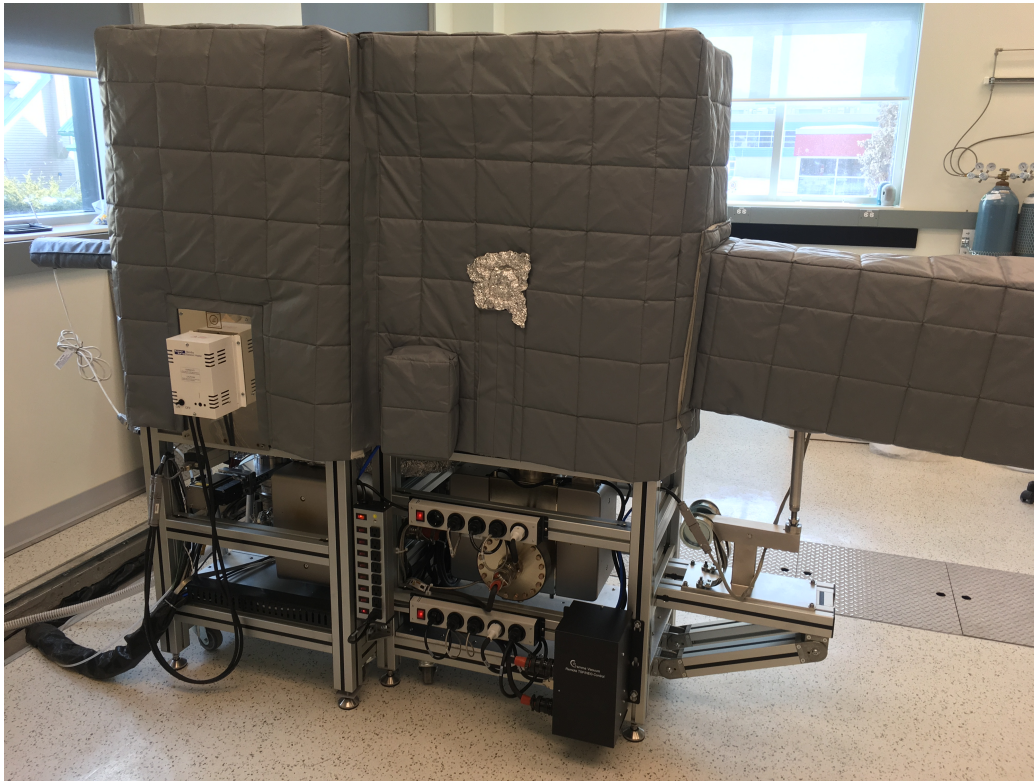


Figure 2: System with all tents visible except wobblestick cover (it is on the opposite side), with transfer arm on the left and manipulator arm on the right.

12. Check all plugs before continuing. Power bar switches should be lit up if switched on:
 - ☐ Plug in the heater and its fan into the associated plugs (labelled "Heater" and "Fan 1").
 - ☐ Plug in the transfer arm plug to its associated plug (labelled "Transfer Arm").
 - ☐ The SPM power strip (Figure 3) has the following plugs:
 - (i) Empty.
 - (ii) Preparation Chamber TSP.
 - (iii) Bypass valve heater.

- (iv) SPM TSP.
- (v) SPM ion pump.
- ☐ The Load lock power strip (Figure 3) has the following plugs:
 - (i) Transfer arm heater.
 - (ii) Power well heater 1.
 - (iii) Power well heater 2.
 - (iv) Preparation chamber ion pump.
 - (v) Finbar.



Figure 3: SPM (top) and Load lock (bottom) power strips. The plugs run through those listed in Step 11 from left to right.

1.2 Bakeout

1. Do a final check that the system is prepared:
 - ☐ System is at sufficiently low pressure.
 - ☐ Gate valves were opened.
 - ☐ Temperature sensitive parts were removed from the baking area.
 - ☐ Motor was removed from manipulator arm.
 - ☐ All tents were attached and properly fastened together. Aluminium foil covers all other openings.

- ☐ System surfaces were cleaned with IPA.
 - ☐ All heaters were plugged in and in the correct locations, including the heater, fan and transfer arm.
2. Turn on the BCU14 unit. Note for the following that all changes made to settings must be saved in order to take effect.
 - (i) The baking temperature is set to 130°C by default. The temperature must be above 100°C in order to properly bake the system, but should not exceed 145°C, to avoid damage.
 - (ii) Choose the time to bake for by changing both the "regulated out" and "continuous out" settings for both Zones 1 and 2. This timer will begin only once the set temperature is reached.
 - (iii) Set a heating/cooling ramp speed if desired. Note that in the settings "Cooling ramp" is written "Colling ramp". The cooling ramp will only begin once the baking timer is finished.
 - (iv) For Zone 1, make sure the "Interlock" is set to *always off*.
 - (v) For Zone 2, make sure the "Interlock" is set to *always on*.
 - (vi) Push both "On" buttons on the screen to begin the bakeout. They will switch to "Off" buttons and heating elements should be displayed to their right, meaning the process is running.

1.3 After Bakeout

1. Pressure at the end of the bakeout process should be below 10^{-6} Torr, but ideally as low as 10^{-7} Torr.
2. Turn off both ion gauges for both filaments.
3. Turn on the Gamma Vacuum unit.
 - (a) Both Preparation and SPM chamber should read "Standby".
4. Turn on one of the ion pumps (Preparation or SPM Chamber) using the Gamma Vacuum unit.
 - (a) Push and hold to turn on.

- (b) Turn off after a few seconds, or if wide range gauge displays an "HV" pressure of 10^{-4} Torr or lower, or if the voltage displayed is lower than 2500V.
 - (c) Repeat these steps with the other ion pump (SPM Chamber or Preparation).
 - (d) Both ion pumps should be off before proceeding.
5. Turn both ion filaments on.
- (a) Turn on the degas switch for both filaments. These will take 10 minutes to run and automatically turn off.
6. On the Gamma Vacuum unit, prepare the degas program for the ion pumps.
- (a) Use the following settings (menu: TSP config: 2x3 Filament tips).
 - (b) The program will degas each of the six filaments for the "On Time" chosen. The first run for example will then take 840 seconds.

Level (A)	31	36	41	46
On Time (s)	120	90	60	45
Off Time (s)	10	10	10	10

7. Turn on the ion pumps.
8. Turn off Zones 1 and 2 on the BCU14 unit.
9. Run the moving parts around the system.
- (i) Wear heavy duty gloves. The system will still be hot.
 - (ii) Remove the wobblestick cover and open the front face of the SPM tent.
 - (iii) Wobble the wobblestick.
 - (iv) Move the shields around the scanning head.
 - (v) Close and open the gate valves.

10. Shut all valves. Refer to Figure 1 for their locations.

- ☐ Prep. Chamber - Bypass valve.
- ☐ Prep. Chamber - STM isolation valve.
- ☐ Load lock - STM valve.

11. Record the total time of the bake and the final pressure of the system after the bake.

2 Power Zones

	Zone 1	Zone 2
Unregulated	[SPM power strip] ·SPM ion pump (4) ·TSP heaters ·Bypass tubing	[Load lock power strip] ·Prep. ion pump (4) ·Finbar heater ·Transfer arm ·Load lock pump well (bottom, 2)
Regulated	Tent Heater	Load lock top (2)

"Fan 1" is separate from the above and is plugged in to it's own outlet ("Fan 1") in the BCU14 unit.

8.8 Vacuum Annealing Furnace

Statement of Contributions: *Ryan Plumadore designed the system and stage, assembled all elements of the vacuum furnace, and created the procedure outlined below. Scott Wheeler aided with the design of the stage. Ian Meyers aided with the implementation of the temperature controller and wiring.*

An important step in the fabrication of high quality van der Waals heterostructures is annealing. To protect samples from oxidation, this process can be performed either in the presence of forming gas, or in vacuum. While our STM system includes a preparation chamber which can anneal samples in UHV, introducing samples to the preparation chamber interrupts the ongoing STM experiments, and requires that the substrate be affixed to an STM sample plate. In addition, the ultimate temperature the annealing stage in the RHK system can reach for resistive heating is limited by some temperature-sensitive components in the chamber, requiring the use of liquid nitrogen cooling. For these reasons, a tabletop vacuum annealing furnace was designed and constructed.

The vacuum annealing furnace can heat small samples, reaching temperatures above 600°C in a high vacuum environment ($\sim 1\text{E}^{-8}$ Torr). Samples can be introduced directly and positioned onto the heating stage, which holds a small molybdenum button heater. This heater is connected via custom wiring to an electronic feedthrough on the back port, and controlled via a homemade temperature controller unit. High vacuum pressure is achieved with the use of a tabletop unit (Edwards T-Station 85), with a turbo pump attached to the bottom port of the chamber. One of the side ports is connected to a pressure sensor, from which the pump controller reads values directly.

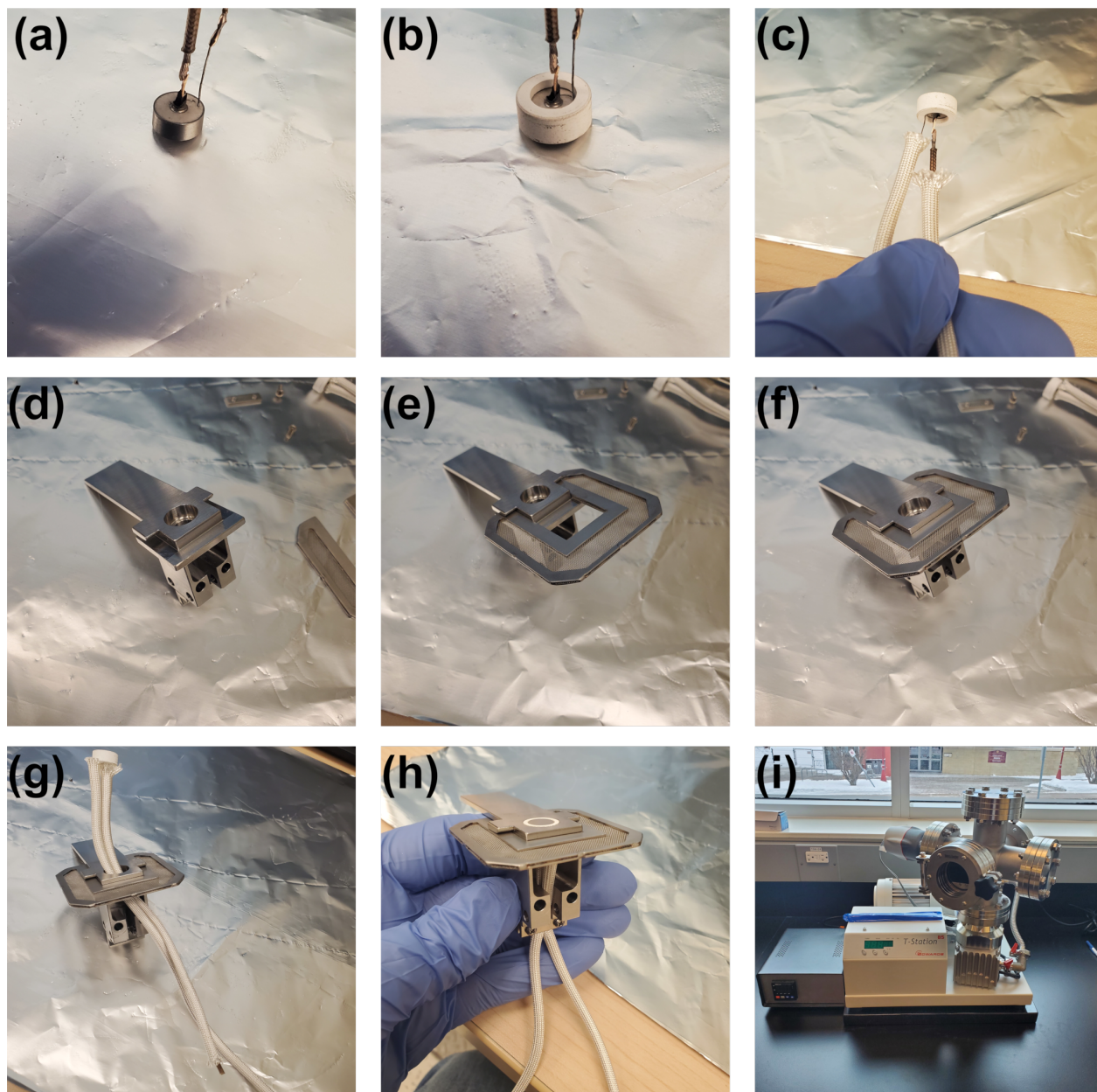


Figure 8.11: Vacuum furnace stage. (a) Custom molybdenum button heater with power supply cable (central wire) and integrated thermocouple (thin wire), which is electrically disconnected from the rest of the stage via the (b) insulating ceramic piece which holds the button heater. (c) Braided insulating sleeves prevent these wires from shorting to the inner walls of the chamber. (d) Custom stage, which protects the wiring and aids in loading samples. (e, f) A stainless steel mesh slides onto the stage and prevents users from dropping samples. (g) The heater element is held by the stage, and (h) the wires are held securely by a clamp at the bottom. (i) The full stage is held in the vacuum furnace chamber, a six-way cross mounted directly onto the TSP of an Edwards T-Station 85.

The vacuum chamber is constrained to the minimal volume required to easily introduce samples, which is done through a fast access viewport door on the front port. The small size of the chamber reduces pump down time and limits the surface area available for rest gases to adsorb onto, an important feature for a system which is exposed to air frequently yet must still achieve high vacuum. The chamber has two additional ports, one on the top and another on the side opposite the pressure sensor. These are capped with blank flanges, but allow flexibility for the system to add on additional components if desired.

Samples are placed on a custom made, stainless steel stage inside the furnace. The stage also houses the homemade electrical components (wiring and thermocouple connections) for the heater. A custom-made ceramic piece electrically isolates the button heater from the rest of the stage. The stage is suspended in the exact centre (the area with the most pumping efficiency) of the chamber via four stainless steel rods. These rods sit on stainless steel cylindrical segments which rest on the bottoms of the four horizontal ports. This mounting scheme is designed such that the stage can be easily removed to adjust wiring or to retrieve samples which may be accidentally dropped in the chamber. An additional feature of the cylindrical segments is to provide a flat base upon which samples can be carefully slid into or out of the chamber, reducing the chance of dropping samples.

8.8.1 Procedure: Operating the vacuum annealing furnace

This guide is a quick reference for standard use of the vacuum furnace.

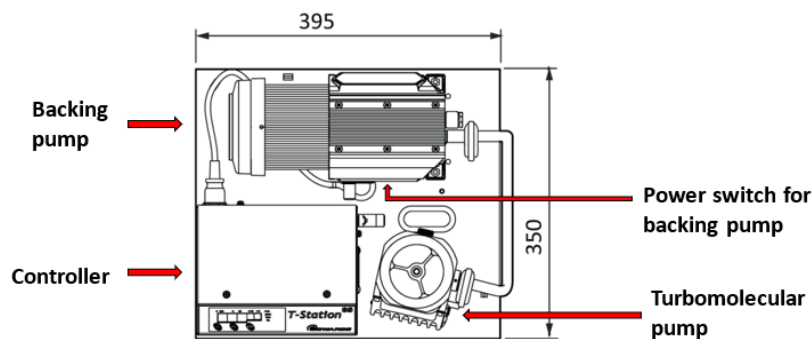
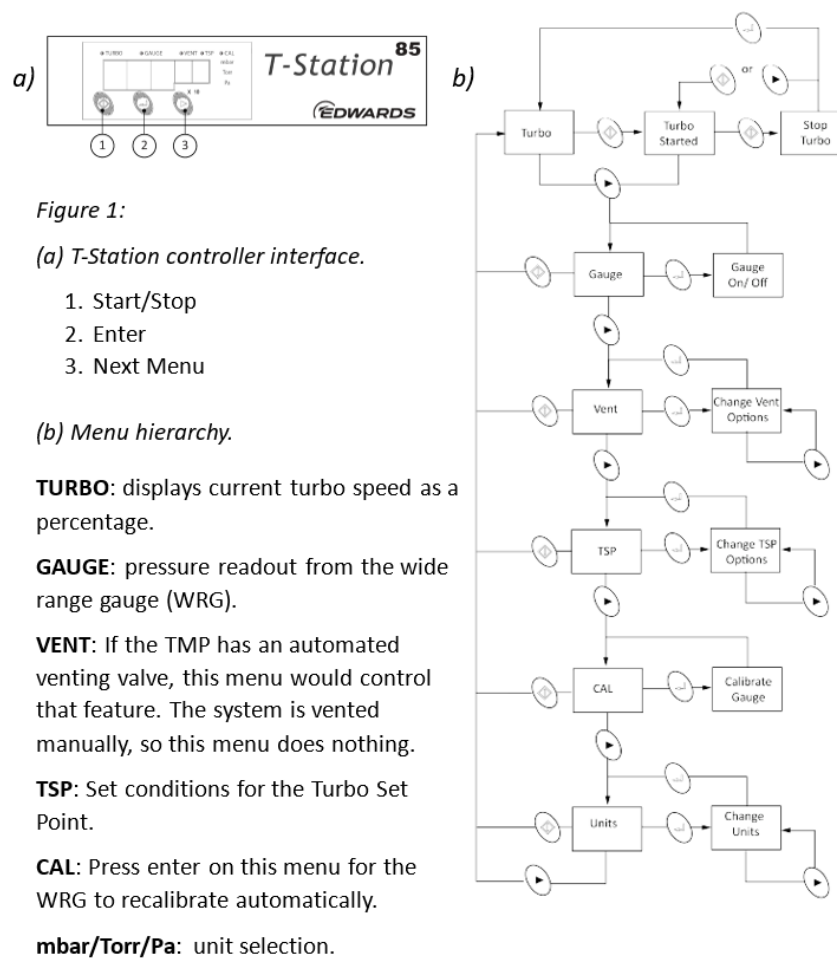


Figure 8.12: Vacuum furnace pumping station diagram, from T-Station 85 Instruction Manual. (a) T-station controller interface. (b) Menu hierarchy flowchart. (c) diagram of the pumping station from above (units in mm).

1. Ensure the system (TMP, backing pump, button heater) is off, and vented to atmospheric pressure (760 Torr).
2. Unscrew and swing open the front port, load your sample directly onto the button heater, and then screw the front port shut again.
3. Ensure the vent valve on the back of the turbo pump is closed tightly. Check that the Turbo Set Point (TSP) is set to 6 Torr. Check that the power switch for the backing pump is set to the on position.
4. Press START: The backing pump will begin pumping the system down to roughly 5 Torr. The TMP will not start until the setpoint is reached. Once the pressure reads below 10^{-5} Torr (i.e. 9×10^{-6} Torr or lower), you can proceed.
5. IMPORTANT: Do not move any part of the setup while the TMP blades are spinning or the pumps are running; this could lead to a catastrophic failure. Do not open the vent valve on the back of the TMP or the front port of the chamber while the pumps are running. Do not remove or unplug the pressure gauge while the system is on.
6. The top left portion of the % sign on the display flashes to indicate acceleration of the TMP and stops when the TMP reaches 80% of its maximum speed. The TMP should reach its full rotational speed in 150-200 seconds. (If a turbo setpoint has been set the flashing will continue until the setpoint is reached, after which the TSP LED turns off).
7. Ensure the thermocouple and power cables are connected to the electrical feedthrough (rear flange of the chamber).
8. Set the desired setpoint (typically 300°C) on the power supply/electrical controller box by manually ramping up the temperature. After the desired annealing time (typically 30 minutes) is complete, slowly ramp down the temperature.

9. STOP: When pumps are running, press the start button. The display will show “Stop” for 3 seconds. Press the Enter key within 3 seconds to confirm. The backing pump will shut off and the TMP will decelerate. The bottom right portion of the % sign will flash until the pump has completely stopped.
10. Do not open the system or vent valve until the TMP has completely stopped. This typically takes 10 minutes. Venting the chamber while the TMP is spinning will cause the blades to abruptly stop, which damages the TMP and reduces its lifetime. If the system is venting while the blades are spinning quickly ($> 25\%$ TMP speed) they may shatter.
11. Manually shutting off the TMP (only if there is an electrical failure): Keep the backing pump on for the following step, until the TMP is completely stopped. Turn off the backing pump before unscrewing the front port.
12. Venting: With the TMP off and $< 5\%$ speed, open the vent port valve very slightly then close it again immediately. Continue flushing the system in this way until the TMP is completely stopped and the pressure reaches 0.1 Torr. Unscrew the front port and open the vent port valve until the system reaches atmospheric pressure (760 Torr) or until the front port pops open.
13. Remove your sample. If you are finished with the vacuum furnace, close the front port and screw it shut. Start the pumps to bring the chamber pressure down below 1×10^{-5} Torr, then shut off the pumps and leave the system sealed and under vacuum.