

Scanning tunneling microscopy investigations of interlayer interaction induced superstructures in transition metal dichalcogenides

by

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Declaration of Authorship

I hereby certify that this thesis and the works presented in it are entirely my own except where otherwise indicated. I am aware of the University of Ottawa's regulations concerning plagiarism. Parts of this work have been published before, in particular, sections of Chapters 4 and 5, and figures in Chapter 6 have been published in academic journals with co-authors, and are repeated here with some modifications. The contributions of myself and others to relevant chapters of this thesis are stated below.

Chapter 4 – This chapter reproduces the paper **L. Molino, L. Aggarwal, V. Enaldiev, R. Plumadore, V.I. Fal'ko, A. Luican-Mayer. "Ferroelectric switching at symmetry-broken interfaces by local control of dislocations networks". *Adv. Mater.* 35, 38, 2207816 (2023).** The experiments in this work were suggested by Adina Luican-Mayer (A.L.-M.). The samples were prepared by Laurent Molino (L.M.). The data was collected and analysed by L.M. and Leena Aggarwal (L.A.), with advice from Ryan Plumadore (R.P.), using software written by L.M.. The COMSOL calculations were performed by L.M.. Vladimir Enaldiev and Vladimir I. Fal'ko provided the theoretical model and contributed to the interpretation of the data. The manuscript was drafted by L.M. and edited by all authors.

Chapter 5 – This chapter reproduces the paper **L. Molino, L. Aggarwal, I. Maity, R. Plumadore, J. Lischner, A. Luican-Mayer. "Influence of atomic relaxations on the moiré flat band wavefunctions in antiparallel twisted bilayer WS₂". *Nano Lett.* 23, 24, 11778–11784 (2023).** The experiments in this work was planned by A.L.-M and L.M.. The samples were prepared by L.M. The data was collected and analysed by L.M. and L.A., with advice from R.P., using software written by L.M.. Indrajit Maity and Johannes Lischner provided the first principles calculations and contributed to the interpretation of the data. The text was drafted by L.M. and L.A. and edited by all authors.

Chapter 6 – This chapter reproduces figures from the paper **S. Ramos, B. Carvalho,**

R.L.M. Lobato, J. Ribeiro-Soares, C. Fantini, H. Ribeiro, L. Molino, R. Plumadore, T. Heinz, A. Luican-Mayer, M. Pimenta. "Selective electron-phonon coupling in dimerized 1T-TaS₂ revealed by resonance Raman spectroscopy". *ACS Nano* 17, 16, 15883–15892 (2023). L.M. and R.P. prepared the sample used for STM/STS. L.M. collected and analysed the scanning tunneling microscopy data with the advice and assistance of R.P..

Abstract

In vertically stacked two-dimensional (2D) materials, interlayer interaction can lead to the formation of superstructures, with properties not present in their constituent parts. These superstructures give rise to new phases of matter, such as charge density waves (CDW), and the many-body physics arising from dispersionless bands in moiré systems. The transition metal dichalcogenides (TMDs) have been of particular recent interest due in part to their reduced symmetry compared to graphene, and their capacity, in the twisted bilayer case, to host nearly dispersionless bands over a broad range of angles.

In this thesis, scanning tunneling microscopy (STM) is used to study emergent superstructures in TMDs. A procedure is developed for the fabrication of STM-compatible twisted TMD samples. Using this procedure, a series of samples are produced to study the structural and electronic properties of twisted bilayer WS_2 in different moiré regimes. In these samples, we observe in-plane structural reconstruction leading to ferroelectric stacking order domains. We demonstrate local control of the domain wall bending with the STM, and explore the role of anisotropic strain in the domain wall network dynamics. Subsequently, we study a sample in the unreconstructed moiré regime, investigate the role of out-of-plane relaxation on the flat band wavefunctions, and through comparison to first principles techniques, present evidence for the suppression of the moiré buckling in our sample. In addition to the moiré results, the commensurate CDW phase of 1T-TaS₂ is observed with STM, and broad spectrum density of states measurements are used alongside Raman spectroscopy to argue for selective electron-phonon coupling and interlayer dimerization in this system.

These results contribute to the understanding of the structural and electronic properties of TMDs, moving the field forward toward device applications, including establishing twisted

transition metal dichalcogenides as a platform for quantum simulation.

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List of Publications

Note: from the list below, items three to five are included in this thesis.

1. **Laurent Molino**, Xueying Li, Sean Walker, Ryan Plumadore, Patrick Sarsfield, Kenji Watanabe, Takashi Taniguchi, Vladimir I. Fal'ko, Adina Luican-Mayer. "Reconstruction domains in heterostructures of twisted monolayer-bilayer graphene". In preparation.
2. **Laurent Molino**, Ryan Plumadore, Leena Aggarwal, Xueying Li, Alexandre Imbert, Jonathan Brunette, Adina Luican-Mayer. "Scanning Probe Microscopy Studies of van der Waals Heterostructures – Twisted Transition Metal Dichalcogenides and Beyond". In preparation.
3. **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 ". *Nano Lett.* 23, 24, 11778-11784 (2023)
4. 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". *ACS Nano* 17, 16, 15883–15892 (2023)
5. **Laurent Molino**, Leena Aggarwal, Vladimir Enaldiev, Ryan Plumadore, Vladimir I. Fal'ko, Adina Luican-Mayer. "Ferroelectric switching at symmetry-broken interfaces by local control of dislocation networks". *Adv. Mater.* 35, 38, 2207816 (2023)

List of Abbreviations

Abbreviation	Definition	Page
2D	Two-Dimensional	v
AP	Antiparallel	3
BZ	Brillouin Zone	71
CB	Conduction Band	72
C-CDW	Commensurate Charge Density Wave	93
CBE	Conduction Band Edge	72
CDW	Charge Density Waves	v
DFT	Density-Functional Theory	76
DOS	Density of States	13
DW	Domain Wall	38
DWN	Domain Wall Network	38
hBN	Hexagonal BN	25
IC-CDW	Incommensurate Charge Density Wave	95
LDOS	Local Density of States	8
LT	Low-Temperature	20
MATBG	Magic Angle Twisted Bilayer Graphene	2
MBA	Modified Bardeen Approach	12
NC-CDW	Nearly Commensurate Charge Density Wave	95
P	Parallel	3
PDMS	Polydimethylsiloxane	27
PLD	Periodic Lattice Distortion	94
PPC	Polypropylene Carbonate	27
PSD	Perfect Screw Dislocation	60
PVD	Physical Vapour Deposition	25
RGA	Residual Gas Analyser	18
RT	Room-Temperature	20
SOP	Standard Operating Procedure	24
STM	Scanning Tunneling Microscopy	v
STS	Scanning Tunneling Spectroscopy	6
TMD	Transition Metal Dichalcogenide	v
TMP	Turbomolecular Pump	19
TSP	Ti Sublimation Pump	22
tTMD	Twisted Transition Metal Dichalcogenide	24
VB	Valence Band	72
VBE	Valence Band Edge	72
vdWH	van der Waals Heterostructures	1

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Chapter 1

Introduction

In this chapter, the state of the field of two-dimensional (2D) materials is discussed with a focus on moiré physics, providing context for this work.

1.1 Two-dimensional materials and new phases of matter

2D materials are layered crystals in which the atoms within a layer are held together by covalent bonds, while the layers themselves are bound together vertically by the van der Waals interaction [1–3]. Since the first exfoliation of graphene in 2004 [4], and the first exfoliation of a transition metal dichalcogenide (MoS_2) in 2005 [5], producing few-layer and monolayer 2D material samples has become routine and inexpensive. Furthermore, a wide variety of 2D materials are now available, including metals [6–8], semi-conductors [9–12], insulators [13–15], magnetic materials [16–19], and superconductors [5, 20–22]. These advancements have allowed for the exploration of the new phases of matter present in layered crystals, including topologically non-trivial band structures [23–25], interlayer excitons [26, 27], and many body physics [28–38].

Now-standard fabrication techniques [39–44] allow for the fabrication of 2D material heterostructures (also called van der Waals heterostructures (vdWH)) by vertical stacking of 2D crystals. These techniques allow for the combination of different materials, and control over interlayer twist angles, giving experimenters a multidimensional parameter space

for band structure engineering. The root of the interest in these systems is interlayer interactions. Interlayer interactions lead to novel properties not present in the heterostructure's constituent elements, the whole being greater than the sum of its parts in terms of both atomic and electronic structure [1–3, 45].

1.1.1 Moiré patterns and magic angle graphene

A key interlayer interaction, which has attracted intense interest in recent years, is the formation of a moiré pattern [46–48]. Observed experimentally with scanning tunneling microscopy (STM) as early as 1990 [46, 49, 50], a moiré pattern is a superstructure of alignment and misalignment between two crystal lattices, typically owing to a small lattice constant mismatch, and/or a marginal interlayer twist. The most prominent result in moiré physics has been the discovery of nearly dispersionless bands in bilayer graphene twisted at the "magic" angle of 1.1° . Magic angle twisted bilayer graphene (MATBG) was first predicted in 2011 [51, 52], and was realised experimentally in 2018 [53]. Dispersionless bands lead to enhanced electron-electron interactions, including an insulating to superconducting transition at certain filling factors [32]. Since that time, work on bi- and multilayer graphene has proliferated, leading to the identification of new correlated and topological phases in twisted systems [24], and structural reconstruction phenomena [28, 54–60], sometimes leading to quasi crystallinity in multilayer systems [61], as well as recent interest in dispersionless bands in untwisted rhombohedral stacked graphene [62–65].

1.1.2 Transition metal dichalcogenides

Work on 2D materials and moiré physics has not been limited to graphene; the transition metal dichalcogenides (TMDs) have been the focus of intense recent interest.

TMDs are 2D materials with formula MX_2 (M = metal, X = chalcogen). The most broadly studied are the hexagonal TMDs, namely those with a $P6_3/mmc$ or $R3m$ structure, in par-

ticular WS_2 , WSe_2 , MoS_2 and MoSe_2 [66–69]. As shown in Figure 1.1, they feature a honeycomb lattice with the transition metal on one sublattice and the pair of chalcogens on the other, giving them only three-fold symmetry as compared to graphene, and a lack inversion symmetry in the monolayer case. Monolayers of the hexagonal TMDs are direct band gap semiconductors [70] with high spin-orbit coupling [71] and are of interest for transistor and optical applications [72–75].

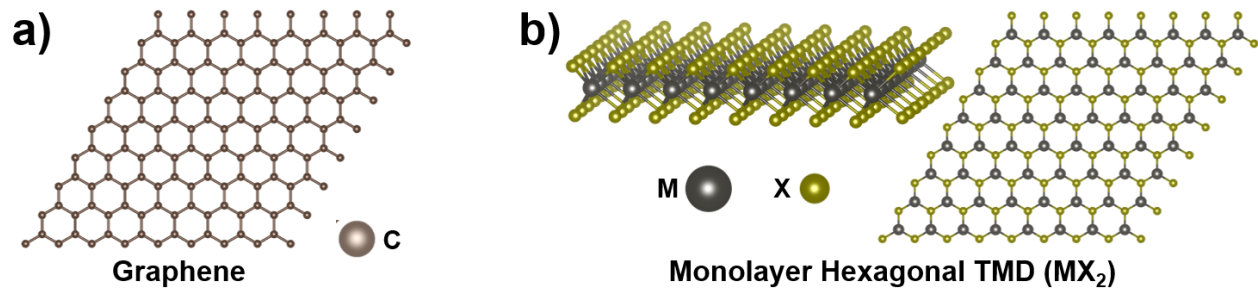


Figure 1.1: Schematic of (a) Monolayer graphene (b) Monolayer hexagonal TMD

Beyond the monolayer, twisted bilayer TMDs have characteristics that make them attractive candidates to build on the moiré physics work on twisted bilayer graphene. While there are important similarities, TMDs behave in ways distinct from graphene, owing to their reduced symmetry, and, in most cases, semiconducting band structures.

Marginally twisted bilayers of hexagonal TMDs can be divided into parallel- (P-) aligned bilayers, in which the armchair directions of the two layers (or equivalently the zig-zag directions) have a relative misalignment marginally off of 0° , (or equivalently 120° or 240° due to the three-fold symmetry of the lattice), and antiparallel- (AP-) aligned bilayers, in which the armchair directions have a relative misalignment marginally off of 180° (or equivalently 60° or 300°). AP alignment tends to be the natural stacking for the hexagonal TMDs [76].

A key variable in determining how a moiré pattern forms is whether the bilayer consists of two layers of the same material (homobilayer) or two layers of different materials (heterobilayer). In homobilayers, the misalignment between the two lattices producing a moiré

pattern is entirely due to the twist angle, while in heterobilayers the differences in the unit cell parameters also contribute to the lattices' misalignment. The formula for the period λ of a moiré pattern in two hexagonal 2D materials is given by Equation 1.1 [77].

$$\lambda = \frac{(1 + \delta)a}{\sqrt{2(1 + \delta)(1 - \cos\phi) + \delta^2}} \leq \frac{1}{\delta} + a \quad (1.1)$$

Here, a is the lattice constant of one material, δ is the fractional lattice mismatch, and ϕ is the interlayer twist angle. The period increases with decreasing twist angle. For heterobilayers, at small twists the effect of the lattice mismatch becomes dominant, imposing an upper limit on the moiré period. As is shown in Equation 1.2 and Figure 1.2, for homobilayers there is no lattice mismatch, and therefore there is no upper limit on the moiré period.

$$\lambda = \frac{a}{\sqrt{2(1 - \cos\phi)}} \leq \infty \quad (1.2)$$

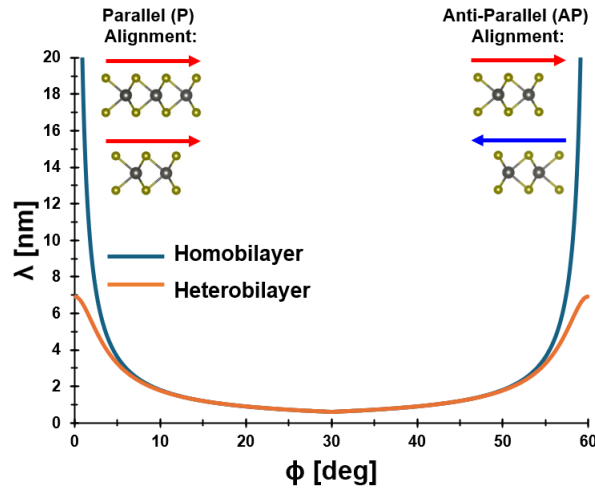


Figure 1.2: Moiré period as a function of twist angle for homobilayer (WS_2/WS_2) and heterobilayer (WS_2/WSe_2) TMDs.

This dynamic has had important implications for experimental work on these systems. In heterobilayers, the lattice mismatch results in a moiré period which is less sensitive to

the twist angle, and therefore easier to control. For this reason, early work focused on heterobilayers with limited moiré wavelengths [34, 35, 78–84]. However, homobilayers are now emerging as the primary focus of scanning probe work [36, 85–93], in part due to growing interest in phenomena which emerge at long moiré wavelengths.

In long moiré period homobilayer systems, major in-plane reconstruction and the formation of stacking order domains has been observed [88, 89, 94–101]. In Chapter 4, we will examine how the reduced symmetry of bilayer TMDs leads to multiple phases of structural reconstruction as a function of twist angle, as well as a permanent electric dipole associated with some stackings. Results will be presented that demonstrate local control over the stacking order by coupling a scanning tip to the surface electric dipole moment, along with as a theoretical model capturing this behavior.

Electronically, twisted bilayer TMDs have been shown to host flat bands over a much broader range of twist angles than MATBG [102–104], making them strong candidates for the development of quantum simulators (devices to realize computationally intractable quantum mechanical models, such as the Hubbard model) with tunable parameters [34, 105, 106]. In Chapter 5, we will consider the factors that influence the electronic structures of twisted bilayer TMDs, examine how they lead to the emergence of flat bands, and focus on the role of out-of-plane relaxation on the flat band localisation. Evidence will be presented for suppression of out-of-plane relaxation in experiments as compared to standard first principles techniques.

1.1.3 Other transition metal dichalcogenides superstructures: charge density waves in 1T-TaS₂

Moiré patterns are not the only superstructures present in TMDs. In certain materials [107, 108], electron-electron interactions give rise to a long-range ordering called a charge den-

sity wave (CDW) [109–111]. A CDW consists of a periodic modulation of the valence electron density, akin to a standing wave. This standing wave is accompanied by a periodic distortion of the atomic lattice, thus forming a superstructure. While distinct from the moiré physics discussed above, CDW states represent another key phase of matter presented in some 2D systems [112].

In Chapter 6, STM results are present for the commensurate CDW phase of 1T-TaS₂. When paired with other techniques [113], these results provide evidence for electron-phonon coupling and layer dimerization. This latter result is another demonstration of the importance of interlayer coupling in 2D material physics.

1.2 Experimental techniques

The results presented in this work largely consist of scanning tunneling microscopy (STM) and spectroscopy (STS) experiments. In STM, an atomically sharp tip is raster scanned over the surface of a sample while an applied bias drives a tip-sample tunneling current. Variation in the tunneling current with tip height allows for structural and electronic characterization of the surface in real space. In STS, the dependence of the current on the bias is measured to determine the local density of states at the tip-sample junction.

STM is a natural choice for studying superstructures in 2D materials as it allows for structural and (through STS) electronic characterization at the nanometer scale. Furthermore, unlike transport measurements, scanning probe techniques tolerate twist angle disorder, as the local twist can generally be determined from the moiré wavelength. For these reasons, STM has been used extensively to study moiré physics [34–36, 78–93] and CDWs [113–118] in TMDs. However, STM also faces unique challenges, including an extremely high standard of sample cleanliness, and the necessity that the surface of the sample be exposed and electrically contacted.

In Chapter 2, the theory of STM is discussed, along with practical challenges and solutions associated with achieving clean, high-resolution measurements. A description of the instrument and procedures used in this work is also presented. In Chapter 3, the development of a procedure for the fabrication of STM-compatible twisted 2D material samples is presented, along with work towards the development of a backgated sample for quantum simulation.

Chapter 2

Scanning tunneling microscopy and spectroscopy

In this chapter, we discuss the theory of scanning tunneling microscopy (STM) and spectroscopy (STS), along with the theoretical limits on their resolution. We will then discuss technical solutions to the experimental challenges faced in an STM experiment.

2.1 Theory of scanning tunneling microscopy

First developed by Gerd Binnig and Heinrich Rohrer in 1986 [119, 120], STM allows for structural and electronic characterisation of the surface of materials with atomic-scale spatial resolution. An STM experiment consists of an atomically sharp tip in close proximity to the surface of a sample. A (typically constant) bias is then applied between the tip and the sample. This bias induces a quantum mechanical tunneling process, which leads to a tunneling current between the tip and sample. Using piezo-electric motors, the tip is raster-scanned over an area, measuring the current at a grid of points, producing a map of tunneling current as a function of position. This is typically referred to as a constant height STM topography map. Since the tunneling current is dependent on the tip-sample distance and the local density of states (LDOS), these topography maps are sensitive to both structural changes in the underlying material, such as layer step edges and variation

in surface height, as well as electronic changes, such as spatial density variations in the free-electron wavefunctions and atomic orbitals, the latter of which allows for the resolution of the surface atomic lattice. In practice, it is more typical to take STM topography maps using a feedback loop which maintains a set-point tunneling current. As the tip scans, the loop adjusts the tip height to keep the tunneling current constant. This is a constant current STM topography map. In the constant current case, the measurement can be thought of as a map of a constant-tunneling iso-surface.

STM can also be used to access the LDOS of the sample surface by measuring the dependence of the tunneling current on the applied bias. This technique is called scanning tunneling spectroscopy. When STS is combined with raster scanning, it allows for the imaging of sample wavefunctions at a given energy in real space.

2.1.1 One-dimensional model of tunneling

The principle of STM can be derived from a simple one-dimensional quantum mechanical argument. Consider tunneling across a rectangular barrier, representing the gap between the tip and the sample. Here, E_F^t and E_F^s are the tip and sample Fermi energies respectively. E_{Vac} is the vacuum energy, such that the tip and sample workfunctions ϕ^t and ϕ^s are given by $\phi^{t(s)} = E_{Vac} - E_F^{t(s)}$. For this example, an electric field chosen to equalise the Fermi levels of the tip and the sample is applied, making the potential trapezoidal. However, for small fields, we can still treat the barrier as a rectangle with height V_0 which is equal to the average height of the trapezoid.

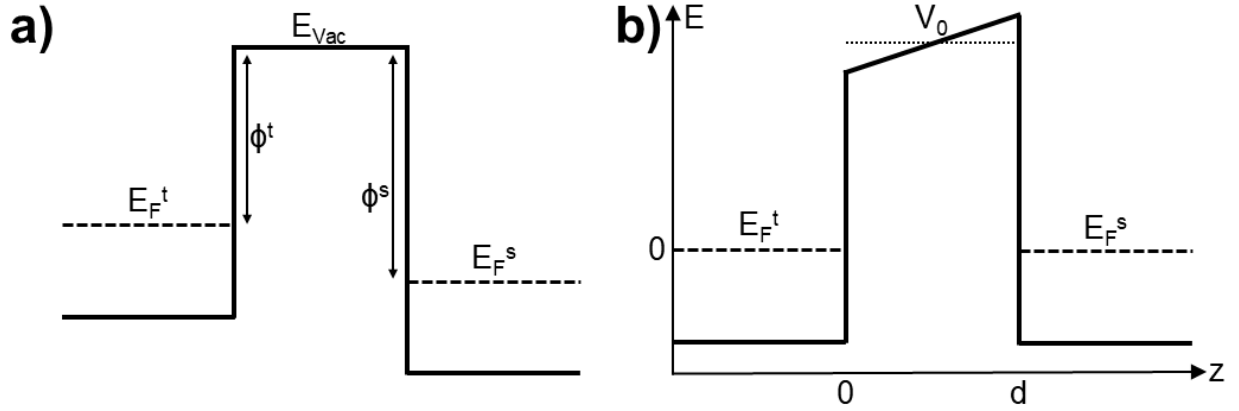


Figure 2.1: Schematic of potential barriers. **(a)** No tip-sample bias is applied. **(b)** Tip-sample bias is applied to equalise Fermi levels.

Taking $E_F^t = E_F^s = 0$ and assuming the electron is incident from the tip, the wave function has the form:

$$\psi(x) = \begin{cases} Ae^{ikz} + Be^{-ikz}, & z < 0 \\ Fe^{\kappa z} + Ge^{-\kappa z} & 0 < z < d \\ Ce^{ikz} & z > d \end{cases} \quad (2.1)$$

with $k = \frac{\sqrt{2mE}}{\hbar}$ and $\kappa = \frac{\sqrt{2m(V_0-E)}}{\hbar}$, where E is the electron energy. The reflection (R) and transmission (T) coefficients are given by:

$$R = \frac{|B|^2}{|A|^2}, \quad T = \frac{|C|^2}{|A|^2} \quad (2.2)$$

This system can be solved by imposing continuity and differentiability at $z = 0$ and $z = d$, and normalization ($R + T = 1$). Using this approach, we find for the tunneling current I :

$$I \sim T \sim e^{-2\kappa d} \quad (2.3)$$

This simple derivation reveals an important property of tunneling which is robust in more

complex models: an inverse exponential dependence of the tunneling current on the tip-sample distance d . In practice, the rule-of-thumb is that tunneling falls off by an order of magnitude per additional Å of tip-sample distance.

2.1.2 Lateral resolution: Tersoff Hamann model

In order to estimate the lateral resolution, we will employ the s-wave model developed by Tersoff and Hamann [121, 122]. In this method, the tip is assumed to be spherical with an entirely s-wave wavefunction. The inverse exponential dependence of current on the z-component of the tip-sample distance is found to hold even in the three-dimensional case.

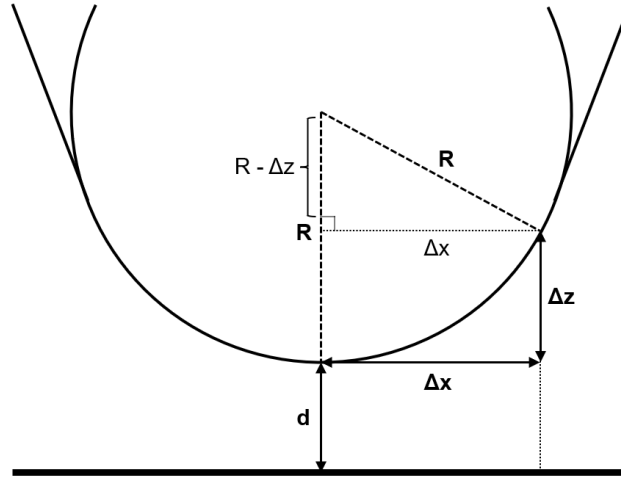


Figure 2.2: Tersoff and Hamann model of lateral tip resolution.

Using the Tersoff-Hamman model, the change in tip height Δz at a lateral distance Δx from the center of the tip can be determined by recognizing that $(R - \Delta z)^2 = R^2 - \Delta x^2$ [123], thus:

$$\Delta z = R - \sqrt{R^2 - \Delta x^2} \quad (2.4)$$

Thus, the tunneling current to a point on the sample surface at a distance Δx from the

point directly below the center of the tip:

$$I(\Delta x) \propto e^{-2\kappa(d+R-\sqrt{R^2-\Delta x^2})} \quad (2.5)$$

Here, κ is again the wavefunction decay constant in the barrier. The tunneling current drops by an order of magnitude when $\frac{I(\Delta x)}{I(0)} = e^{-2}$. Thus:

$$\begin{aligned} e^{-2} &= \frac{e^{-2\kappa(d+R-\sqrt{R^2-\Delta x^2})}}{e^{-2\kappa d}} \\ -2 &= -2\kappa(R - \sqrt{R^2 - \Delta x^2}) \\ \Delta x &= \sqrt{\frac{2R}{\kappa} - \frac{1}{\kappa^2}} \end{aligned} \quad (2.6)$$

For a conservative value for d and R of $d = 1 \text{ \AA}$, and $R = 10 \text{ nm}$, there will be an order of magnitude tunneling drop-off at a radius of $\Delta x = 4 \text{ \AA}$, allowing for a resolution of $8 \text{ \AA}$.

The Tersoff-Hamman model fails to describe actual STM experiments. While scanning electron microscopy measurements show that tip radii are typically in the range of tens of nanometers, corrugations on the order of $1 \text{ \AA}$ are routinely achieved. This is because STM tips are typically made of d-wave metals such as W, Pt, and Ir, in which the s-wave model does not apply. These metals are able to achieve much better spatial resolutions due to the greater localisation and out-of-plane extent of their wavefunctions.

2.1.3 Modified Bardeen approach

A general expression of tunneling current can be produced using the modified Bardeen approach (MBA) [124, 125]. In the MBA, the probability P of tunneling between an initial state $|i\rangle$ and final state $|f\rangle$ induced by an interaction potential V is given by Fermi's golden rule:

$$P_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle f | V | i \rangle|^2 \delta(E_f - E_i) \quad (2.7)$$

Assuming the tip and sample have the same Fermi level, the tunneling current from tip to sample can be given by an integral over all energies, where the current at each energy ϵ is the probability $P_{t \rightarrow s}$, multiplied the tip density of states (DOS) at that energy $\rho_t(E)$ and the fraction of filled states in the tip given by the Fermi-Dirac distribution $f(E) = \frac{1}{e^{E/k_B T} + 1}$. This integrand is then multiplied by the DOS and the fraction of empty states in the sample:

$$I_{t \rightarrow s} = -e \int P_{t \rightarrow s} \rho_t(E_f + \epsilon) f(E_f + \epsilon) \rho_s(E_f - eV_B + \epsilon) [1 - f(E_f - eV_B + \epsilon)] d\epsilon \quad (2.8)$$

where the argument of the sample DOS ρ_s and associated Fermi-Dirac distribution are shifted by the tip-sample bias eV .

Let us now examine the transition probability factor. In the MBA, we treat the tip potential, U_t as the perturbative potential. If the unperturbed tip and sample wavefunctions are ψ_μ and χ_ν respectively, obeying the time-independent Schrödinger equation:

$$\begin{aligned} (\hat{T} + U_s) \psi_\mu &= E_\mu \psi_\mu \\ (\hat{T} + U_t) \chi_\nu &= E_\nu \chi_\nu \end{aligned} \quad (2.9)$$

then the transition probability becomes:

$$\begin{aligned} P_{s \rightarrow t} &= \frac{2\pi}{\hbar} |\langle \chi_\nu | U_t | \psi_\mu \rangle|^2 \delta(E_\nu - E_\mu) \\ &= \frac{2\pi}{\hbar} |M_{\mu\nu}|^2 \delta(E_\nu - E_\mu) \end{aligned} \quad (2.10)$$

Integrating over the volume of the tip, the matrix element can be expressed as:

$$M_{\mu\nu} = \int_{\Omega_t} \chi_\nu^* U_t \psi_\mu d\tau \quad (2.11)$$

By applying the time-independent Schrödinger equation:

$$\begin{aligned} M_{\mu\nu} &= \int_{\Omega_t} \chi_\nu^* (E_\nu - \hat{T}) \psi_\mu d\tau \\ &= \int_{\Omega_t} \psi_\mu E_\nu \chi_\nu^* - \chi_\nu^* \hat{T} \psi_\mu d\tau \end{aligned} \quad (2.12)$$

In the region of the tip, $U_s = 0$, thus $E_\mu = \hat{T} = -\frac{\hbar}{2m} \vec{\nabla}^2$. Applying Green's theorem:

$$\begin{aligned} M_{\mu\nu} &= -\frac{\hbar}{2m} \int_{\Omega_t} \psi_\mu \vec{\nabla}^2 \chi_\nu^* - \chi_\nu^* \vec{\nabla}^2 \psi_\mu d\tau \\ &= -\frac{\hbar}{2m} \int_{\Sigma} \chi_\nu^* \vec{\nabla} \psi_\mu - \psi_\mu \vec{\nabla} \chi_\nu^* d\sigma \end{aligned} \quad (2.13)$$

where Σ is the boundary of the tip. In this form, it is clear that $|M_{\mu\nu}| = |M_{\nu\mu}|$, thus we just label the matrix element M .

We can then write the tip-to-sample tunneling current as:

$$I_{t \rightarrow s} = \frac{-e2\pi}{\hbar} \int |M|^2 \rho_t(E_f + \epsilon) f(E_f + \epsilon) \rho_s(E_f - eV_B + \epsilon) [1 - f(E_f - eV_B + \epsilon)] d\epsilon \quad (2.14)$$

and equivalently, the sample-to-tip tunneling can be written as:

$$I_{s \rightarrow t} = \frac{-e2\pi}{\hbar} \int |M|^2 \rho_t(E_f + \epsilon) [1 - f(E_f + \epsilon)] \rho_s(E_f - eV_B + \epsilon) f(E_f - eV_B + \epsilon) d\epsilon \quad (2.15)$$

The total tunneling current can be expressed as the difference between the forward and reverse tunneling current:

$$\begin{aligned} I &= I_{t \rightarrow s} - I_{s \rightarrow t} \\ &= \frac{-e2\pi}{\hbar} \int |M_{t \rightarrow s}|^2 \rho_t(E_f + \epsilon) \rho_s(E_f - eV + \epsilon) [f(E_f + \epsilon) - f(E_f - eV_B + \epsilon)] d\epsilon \end{aligned} \quad (2.16)$$

Thus, we have a full three dimensional expression for the tunnelling current. In this

formulation the spatial resolution of the experiment is contained within the tunneling matrix element. Unfortunately, the tunneling matrix element is not generally known, as it depends on the detailed atomic configuration of the end of the scanning tip, which tends to change over time. It is therefore difficult to determine *a priori* spatial resolution in a given STM experiment.

2.2 Theory of scanning tunnelling spectroscopy

STS allows for measurement of the LDOS by examining the derivative of the tunneling current with respect to bias voltage. In order to derive this relationship, we will treat the tunneling matrix element as a constant, and assume that ρ_t is energy invariant about the Fermi level. Applying the change of variables $E' = E - eV$ to Equation 2.16, we can write:

$$I \propto \int \rho_s(E_f + \epsilon) [f(E_f - eV + \epsilon) - f(E_f + \epsilon)] d\epsilon \quad (2.17)$$

It thus follows that, taking the derivative with respect to eV_B :

$$\begin{aligned} \frac{dI}{deV_B} &\propto \int \rho_s(E_f + \epsilon) \frac{d}{deV_B} [f(E_f - eV + \epsilon) - f(E_f + \epsilon)] d\epsilon \\ &\propto \int \rho_s(E_f + \epsilon) \frac{d}{deV_B} \left[e^{\frac{E_f - eV_B + \epsilon}{k_B T}} - e^{\frac{E_f + \epsilon}{k_B T}} \right] d\epsilon \\ &\propto \int \rho_s(E_f + \epsilon) \left[\frac{-1}{k_B T} \frac{e^{\frac{E_f - eV_B + \epsilon}{k_B T}}}{\left(1 + e^{\frac{E_f - eV_B + \epsilon}{k_B T}}\right)^2} - 0 \right] d\epsilon \\ &\propto \int \rho_s(E_f + \epsilon) \left[\frac{e^{\frac{E_f - eV_B + \epsilon}{k_B T}}}{\left(1 + e^{\frac{E_f - eV_B + \epsilon}{k_B T}}\right)^2} \right] d\epsilon \end{aligned} \quad (2.18)$$

The argument of the integral is thus the DOS of the sample multiplied by a peaked

function centered at eV_B with a full width at half maximum of $3.2k_B T$. Taking the derivative of the current with respect to the bias selects the value of the DOS at eV_B , with an uncertainty on the order of the full width at half maximum. Therefore,

$$\frac{dI}{dV_B} \sim \rho_s(eV_B) \pm 3.2k_B T. \quad (2.19)$$

At $298K$, $77K$ and $8K$, the uncertainties due to temperature are $82meV$, $21meV$, and $2meV$ respectively. The linear dependence of the resolution on temperature demonstrates the necessity of low temperature for identifying fine features in the spectra such as the van Hove singularities associated with flat bands.

Lock-in amplifier Theory

In practice, $\frac{dI(V_B)}{dV}$ is measured by applying a tip bias with an alternating current bias modulation, and using a lock-in amplifier to extract the component in phase with the modulation. Here, we will show how this is equivalent to measuring $\frac{dI(V_B)}{dV}$.

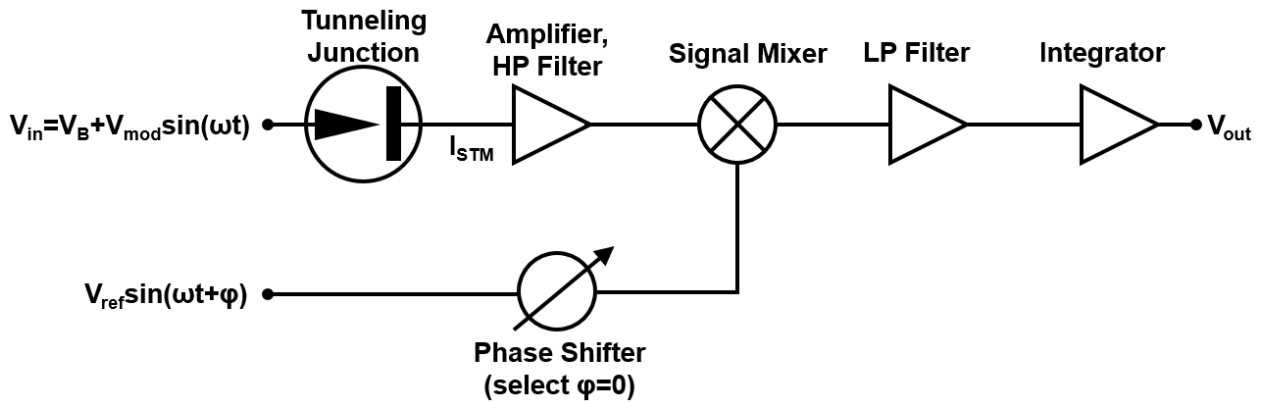


Figure 2.3: Lock-in amplifier schematic.

In response to the input bias $V_{in} = V_B + V_{mod} \sin(\omega t)$, where ω is the frequency of the

bias modulation, the output current can be expressed as a Fourier series.

$$I_{STM} = \sum_{\omega'} c_{\omega'} \sin(\omega' t) \quad (2.20)$$

This signal is then mixed with the reference signal, also of frequency ω , set to be in-phase with the bias modulation. The signal is then integrated, resulting in the output current.

$$\begin{aligned} I_{out} &= \int \sin(\omega t) \sum_{\omega'} c_{\omega'} \sin(\omega' t) dt \\ &\propto \int \sum_{\omega'} \delta(\omega, \omega') dt \end{aligned} \quad (2.21)$$

The integrator attenuates every spectral component not at frequency ω . This has a critical role in noise reduction.

Expressing I_{STM} as a Taylor series, we can thus write

$$I_{STM}(t) = I(V_B) + \frac{dI}{dV_B} V_{mod} \sin(\omega t) + \frac{d^2 I}{dV_B^2} V_{mod}^2 \sin^2(\omega t) + \frac{d^3 I}{dV_B^3} V_{mod}^3 \sin^3(\omega t) + \text{Noise} \quad (2.22)$$

The zeroth order term is removed with a high-pass filter, and the remainder are mixed with the reference frequency $V_{ref} \sin(\omega t)$, thus

$$I_{mixed}(t) \propto \frac{dI}{dV_B} V_{mod} \sin^2(\omega t) + \frac{d^2 I}{dV_B^2} V_{mod}^2 \sin^3(\omega t) + \frac{d^3 I}{dV_B^3} V_{mod}^3 \sin^4(\omega t) + \text{Noise} \quad (2.23)$$

The terms with an odd power of $\sin(\omega t)$ will be removed by the integrator, while higher the even-order terms will contribute to the noise. Neglecting these higher even-order terms, the output signal will be proportional to $\frac{dI}{dV_B}$.

For a single measurement, $\frac{dI}{dV_B}$ is measured over the range $eV_B \pm V_{mod}$, thus the lock-in

measurement has an uncertainty due to the modulation bias of $\pm 2V_{mod}$, though an extra $\pm 0.2V_{mod}$ is typically added to account for the noise. Thus, the total resolution of an STS measurement is given by:

$$\Delta E = \sqrt{(3.2k_B T)^2 + (2.2V_{mod})^2} \quad (2.24)$$

2.3 Practice of scanning tunneling microscopy

In this section, the workflow of an STM experiment as practiced in this work is described, along with more general experimental concerns and some commonly used solutions.

2.3.1 Scanning tunneling microscopy workflow

The STM experiments described in this work were performed with a customised RHK Pan-Scan Freedom STM. As shown in Figure 2.4(a), the system consists of three chambers: a load-lock for transferring tips and samples into the system without opening the system to the environment, a main chamber which houses the STM head and tip and sample "garages", and a preparation chamber equipped for tip and sample annealing and residual gas analysis (RGA) with a quadrupole mass spectrometer.

In a typical experiment, Pt/Ir tips are cut by hand and mounted into tip holders, and the sample is mounted onto a flag-style sample plate with H21D conductive silver epoxy. The STM electronics connect to the sample plate, so it is necessary to have a conductive path from the sample plate to the sample. To load the sample and tip, the load-lock is filled with high purity N_2 . This is to ensure positive pressure when the door is opened to reduce contamination. The load-lock door is then opened to the room, and the tips and samples are loaded onto the manipulator arm with pointed end forceps. The load-lock door is then closed, the N_2 supply is shut off, and the load-lock is pumped down with a turbomolecular

pump (TMP) until it reaches pressures on the order of 10^{-7} Torr , typically overnight. At this pressure, the load-lock can be opened to the main chamber without degrading the vacuum significantly due to its smaller volume. The gate valve to the main chamber can then be opened, the manipulator arm advanced into the main chamber, and the tips and sample transferred with the wobble stick to the tip and sample "garages" for storage, as shown in Figure 2.4(b). The manipulator arm is then retracted and the gate valve is closed.

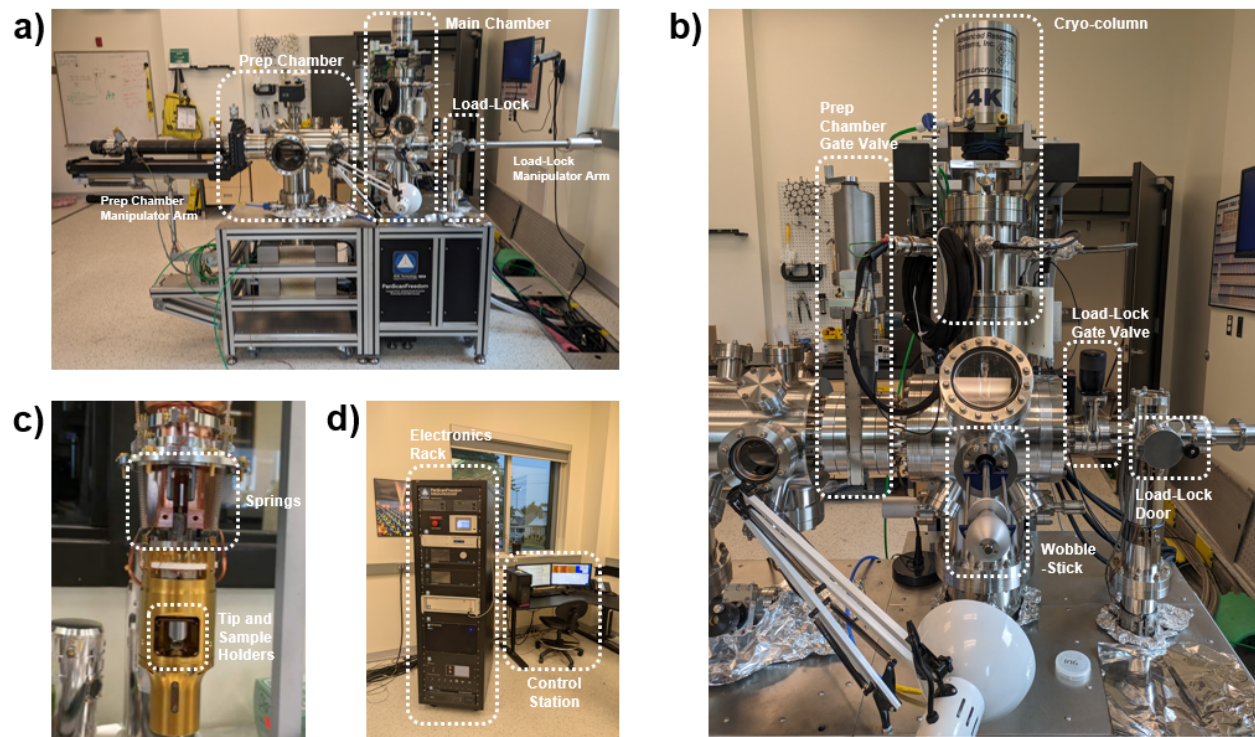


Figure 2.4: Customised RHK Pan-Scan Freedom STM. **(a)** Three-chambered system. **(b)** Main chamber. **(c)** Scanning head. **(d)** Electronics rack and control station. Operator not pictured.

A tip and sample can then be loaded into the STM head for scanning. The STM head is suspended on springs for vibration damping. The head can be "locked" by turning a screw with the wobble stick. This affixes the head to the STM body, taking its weight off of the springs and preventing it from swinging. With the scanning head locked, the sample and tip can then be mounted in the STM head, as shown in Figure 2.4(c). The head can

then be unlocked, allowing it to rest on the springs. The tip can then be aligned with the sample in X and Y using a piezoelectric motor controlled through the system software, and then approached. A camera accessing the system through a window in the back of the main chamber allows for an initial approach on the desired region of the sample, with an accuracy of $\sim 30\mu m$.

Low-temperature experiments

In low-temperature (LT) experiments, it is typical to land on the sample at room-temperature (RT), find the desired region, and take preliminary data before cooling. This is to ensure tip and sample quality, and for easier navigation, since the fine piezo range is greatly reduced at LT.

The cooling system for the RHK Pan-Scan Freedom is a closed-cycle cryostat which consists of a system of He pulse tubes positioned above the STM head in the "cryo-column". These are connected to a He pump, which cycles He to and from the cryo-column. The hot He at the pump exchanges heat with a water cooling system, which then radiates the heat into the air.

To cool the system, the STM head is locked, which brings it nearly in contact with the "cold finger" (the cold end of the cryo-column). The He and water pumps are then turned on, and the He in the system is purged and replaced several times to ensure a good quality cryogen. It is typical to allow several days after cooling has begun before taking measurements to allow for temperature equilibration.

2.3.2 Environmental isolation

In order to take high-quality STM and STS measurements, significant measures must be taken to mitigate thermal broadening and environmental noise; in practice, this means broad spectrum noise dampening, low temperatures, and ultra-high-vacuum pressures.

In this section, we will explore the options for these concerns with reference to the RHK system used for these experiments.

Cryogenics

While achieving good quality STM measurements at RT is possible as demonstrated in the works below, the spectral broadening discussed in Section 2.2 means that low temperature is an absolute necessity for high-resolution STS. Temperatures in the millikelvin range can be achieved with a dilution refrigerator, in which the entropy of mixing of He^3 and He^4 is exploited to achieve cooling. While STM systems using this type of cooling exist, work with them is limited.

Much more broadly used are bath cryostats, in which the system is deposited in a bath of liquid He, allowing for temperatures near the boiling point of $4.2K$ [126]. In these systems, it is necessary to interrupt the experiment when the Helium is boiled off due to the vibrations associated with refilling the system.

Another option, employed in the RHK system in this work, is the closed-cycle cryostat. In a closed-cycle cryostat, a system of pulse tubes cycles He to cool the system. Pulse tubes are heat pumps with no moving mechanical parts at the cool end, making them suitable for LT operation with low vibration. The volume of He is fixed, with losses only due to leaks in the system. The volume of cryogen can also be topped up from an external He supply tank without interrupting the experiment, allowing for continuous low-temperature operation. In the system used in this work, temperatures below $11K$ can be routinely achieved.

Intermediate temperatures can also be used. Some samples are not sufficiently conductive at LT for STM experiments, making intermediate temperatures desirable. In a closed-cycle system, an electric heater can be paired with the cooling system, allowing for arbitrary intermediate temperature operation. Bath cryostats employing liquid N_2 , achiev-

ing temperatures of $78K$, are also a commonly used alternative when LT is not necessary.

Vacuum systems

Pressure is a major concern for STM experiments, both due to the interaction of gas particles with the tunneling junction, and the degradation of unstable samples. Ultra-high vacuum is achieved through a series of pumping mechanisms, each lowering the pressure enough for safe and effective operation of the next. The pressure ranges quoted here are based on experience with the RHK STM system used in this work.

First, pressures of $10^{-2}Torr$ are reached with a roughing pump, in this case a dry scroll pump, which avoids the risk of the hydrocarbon contamination associated with oil. Pressures of $10^{-8}Torr$ can then be reached with a TMP. Pressures of $10^{-9}Torr$ can be reached with an ion pump, which consists of a high-voltage plate that ionizes and holds gas molecules. Ti sublimation pumps (TSPs) can then be used to achieve pressures of $10^{-10}Torr$. A TSP consists of a system to sublime titanium, coating the walls of the chamber and causing gasses to permanently adhere to the surface. TSPs are not in continuous operation but must be "flushed" periodically as the surfaces become saturated. Finally, at low temperatures, cryo-pumping, the process by which gases adhere to the side of the chamber at LT, further lowers the pressure, achieving pressures of $10^{-11}Torr$.

In order to maintain low pressures, the system is never opened to air except for maintenance. New samples and tips are brought through a load lock, which is pumped down with a TMP before being opened to the main chamber. When the chamber is opened to atmosphere, it is often necessary to perform a bakeout: a process by which the system is heated to desorb the particles, in particular water, adhered to the walls, so they can be pumped out all at once, rather than gradually off-gassing over time and degrading the vacuum.

Vibration isolation

Sources of mechanical vibration and electrical noise are plentiful in a laboratory environment, including footsteps ($10^0 Hz$), resonance of the building ($10^1 Hz$), wind, pumps, electronics, and vehicles outside the building ($10^1 - 10^2 Hz$) [125, 127, 128]. In our system, various components attenuate vibration at different frequencies, including the concrete slab on which the STM room sits (which is decoupled from the rest of the building), the rigid STM tables, and critically, the series of coupled springs and masses on which the STM head is suspended. Electrical noise is also a critical concern and can be reduced through the use of low-pass filters and the lock-in amplifier [125, 129]. The bias modulation for the STS is applied at the quietest frequency, which in the case of the RHK system in this work was $1.325 kHz$.

Chapter 3

Fabrication of twisted homobilayers for scanning tunneling microscopy measurement

Advancement in the field of two-dimensional (2D) material physics has been predicated on the development of fabrication techniques for vertically stacked van der Waals heterostructures (vdWHs), and recent advancements can be attributed to improvements in interface and surface cleanliness, and twist angle control. Initial works utilized the "wet transfer" technique, in which 2D materials on polymer are suspended on solvent [15]. However, the standard in the field now is the "dry transfer", in which polymer "stamps" are used to pick up and stack individual crystal flakes [39]. For twisted homobilayer systems, it is typical to use the "tear-and-stack" technique [87, 94, 130–134], in which two halves of the same flake are separated and then stacked to allow for deterministic twist angle control. While existing fabrication techniques now provide a basis for a wide variety of 2D material samples, individual fabrication procedures must be developed to meet the needs of different materials and experimental methods.

In this chapter, the development of a standard operating procedure (SOP) for fabricating twisted transition metal dichalcogenide (tTMD) homobilayer samples for measurement with

scanning tunneling microscopy (STM) is presented, as was applied in the works presented in Chapters 4 and 5. While some details vary (as discussed in Sections 4.3.13 and 5.2.4), the SOP presented here represents best practices as of this writing. This method is also applicable to other materials and can be used to produce multilayer twisted samples, as is demonstrated in as-of-yet unpublished works.

This chapter outlines three phases of development: the initial sample design with a discussion of why it failed (Section 3.1), a successful sample design with detailed SOP (Section 3.2), and work towards a sample design with electrostatic doping capabilities (Section 3.3).

3.1 Initial design: twisted transition metal dichalcogenides on hexagonal BN

In graphene-based vdWHs, hexagonal BN (hBN) is recognized as the ideal substrate due to its wide band gap, few trapped charges and dangling bonds, and atomically planar surface [15, 135]. Motivated by these works, the initial sample design for the twisted homobilayer TMD samples consisted of a twisted bilayer TMD on an hBN substrate, as shown in Figure 3.1(a). hBN is an insulator, and therefore will not carry current to the tTMD, therefore it is necessary to provide an electrical contact. For this reason, the stack is topped with a few-layer graphene flake in contact with the tTMD, and a Ti/Au electrode. The graphene is necessary for a good electrical connection due to the large Schottky barrier associated with the TMD-Au contact [136–139]. The Ti/Au cap also serves to cover up the hBN to prevent accidentally scanning on it, as this would fail to produce a tunneling current, leading to a tip crash. The sample is assembled on a Ti/Au coated Si/SiO₂. These samples were produced using the tear-and-stack method, and the Ti/Au caps were patterned with electron-beam lithography and deposited with physical vapor deposition (PVD).

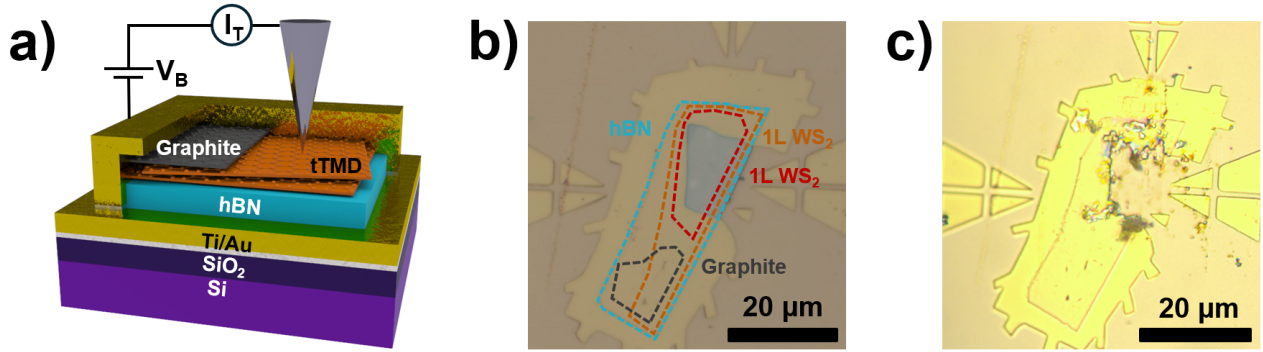


Figure 3.1: Initial tTMD sample design. **(a)** Experimental schematic of the initial sample design. **(b)** Optical micrographs of an example twisted WS₂ samples. **(c)** Optical micrographs of the sample (b) after experiment showing damage due to tip crashes.

A series of samples following this design was produced, as shown in Figure 3.1(b), all of which were damaged before yielding data. In each case, the tip crashed when attempting to scan the tTMD, resulting in the destruction of the sample, as shown in Figure 3.1(c). Later samples in the series were produced with smaller windows in the Ti/Au caps, to ensure that the tip crashes were not due to scanning on exposed areas of hBN. This modification failed to prevent tip crashes.

The reason for these failures is that the TMDs used in these experiments are semiconducting, and over distances of microns the total in-plane resistance becomes too high to produce the set-point tunneling current. In the samples following the initial design, the high in-plane resistance led to tip crashes due to an incomplete feedback loop.

In the literature, hBN substrates have been used for STM experiments on tTMD samples [34, 34–38, 91]. However, in these works, the scanning is either performed near the edge of a graphene layer, or the sample is encapsulated with few-layer graphene etched with nano-ribbons (allowing for scanning between ribbons) or a graphene sensing layer. By reducing the distance between the tunneling junction and the nearest graphene-TMD interface, the total resistance can be kept low enough to achieve the set-point current.

In other STM works [83, 86, 87], the hBN substrate is substituted with graphite to allow

for direct electrical contact. This is the approach that was used in the next generation of samples, described below.

3.2 Successful samples: twisted transition metal dichalcogenides on graphite

Following the attempts described above, a new recipe was developed, consisting of twisted bilayer TMD on graphite, on a Ti/Au coated Si/SiO₂ substrate as shown in Figure 3.2. In this section, a detailed fabrication SOP is outlined, from initial crystal exfoliation to sample cleaning.

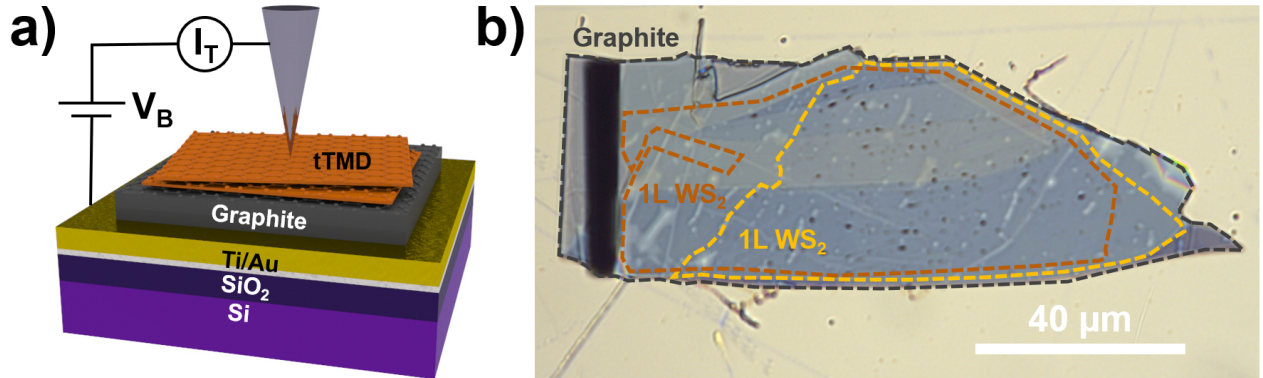


Figure 3.2: Standard tTMD sample design. **(a)** Experimental schematic of sample design. **(b)** Optical micrograph of an example twisted WS₂ sample which follows this design. More optical micrographs in Figure 4.4.

3.2.1 Fabrication standard operating procedure

The stamp assembly

To fabricate 2D material heterostructures with the dry transfer tear-and-stack technique, it is necessary to produce "stamps" capable of adhering to 2D material flakes and peeling them off of their substrates. The stamp assembly used in this work consisted of thin films of polypropylene carbonate (PPC) covering a thicker square of polydimethylsiloxane (PDMS),

fixed to a glass slide using tape "frames", as shown in Figure 3.3(a). The slide is used for mounting in the transfer station as described in [140]. The PPC acts as an adhesive surface, while the PDMS acts as a "pillow", compressing as the stamp is brought into contact with 2D material flake and substrate, allowing for better conformity of the stamp to the 2D material, and control over the substrate-stamp interface. In practice, the stamp assembly is angled such that, as it approaches the substrate, the two contact first only in the corner of the PDMS, with the area of contact increasing as the stamp is further approached. The "fringe" of the contact area is visible with an optical microscope and predictably moves across the substrate as the stamp is approached. It is thus possible to control what areas are contacted with the stamp and which are not, which is necessary for interface cleanliness as discussed below.

Flake exfoliation

To assemble the tTMD on graphite sample, flakes must first be prepared. Graphite is prepared through mechanical exfoliation [4, 5]. A piece of bulk graphite crystal is placed on tape, which is then folded over on itself until a substrate-sized region is covered in crystal. More tape is then used to peel off layers of graphite, thinning it down to the appropriate thickness. The tape is then pressed against a SiO_2/Si substrate and peeled off, leaving behind a random assortment of crystal flakes, of various sizes and thicknesses. From there, an appropriate flake is identified optically (Figure 3.3(b)). The graphite flake must be relatively uniform, and of appropriate shape and size to be mostly covered by the TMD monolayer that it will be used to pick up, to make it easier to navigate to a bilayer region when scanning with STM. Graphite flakes must also be sufficiently thick to screen the surface texture of the Au film on their final substrate ($\gtrsim 20\text{nm}$), but not so thick that scanning over the step edge risks crashing the tip ($\lesssim 60\text{nm}$).

TMD monolayers are prepared using a similar procedure. For the TMDs, once the tape

is covered with an appropriate thickness of crystal, it is then pressed against a square of PDMS cut from a gel pack. The tape is then peeled off, transferring crystal to the PDMS. The PDMS is pressed against a clean SiO_2/Si substrate. The PDMS and substrate are then heated to 80°C on a hot plate. This changes the adhesive properties of the PDMS, facilitating transfer to the substrate when the PDMS is peeled off. Note that this technique has not been observed to be effective for graphite. Monolayers are then identified optically based on colour (Figure 3.3(c)). Their thicknesses are later confirmed with atomic force microscopy (AFM).

van der Waals heterostructures fabrication

To assemble the 2D material stack, each layer is picked up with the PPC/PDMS stamp in sequence, from the bottom up. Picking up graphite is often a low-yield process; best results are achieved when the graphite is exfoliated within eight hours of pick-up. To pick up graphite, the substrate is placed on the transfer station stage and heated to 40°C . The stamp is then brought into contact with the graphite, slowly enough to reduce the formation of bubbles at the interface, and left in contact for several minutes (Figure 3.3(d)). The stamp is then lifted quickly to peel off the graphite (Figure 3.3(e)).

In twisted homobilayer TMDs, the phenomena of interest arise from interlayer interactions, therefore maintaining the cleanliness of the TMD-TMD interface is of critical concern. It is assumed that the TMD crystal is cleaved in the exfoliation process, leaving its surface untouched. It is necessary not to contaminate the surface by contacting it with polymer.

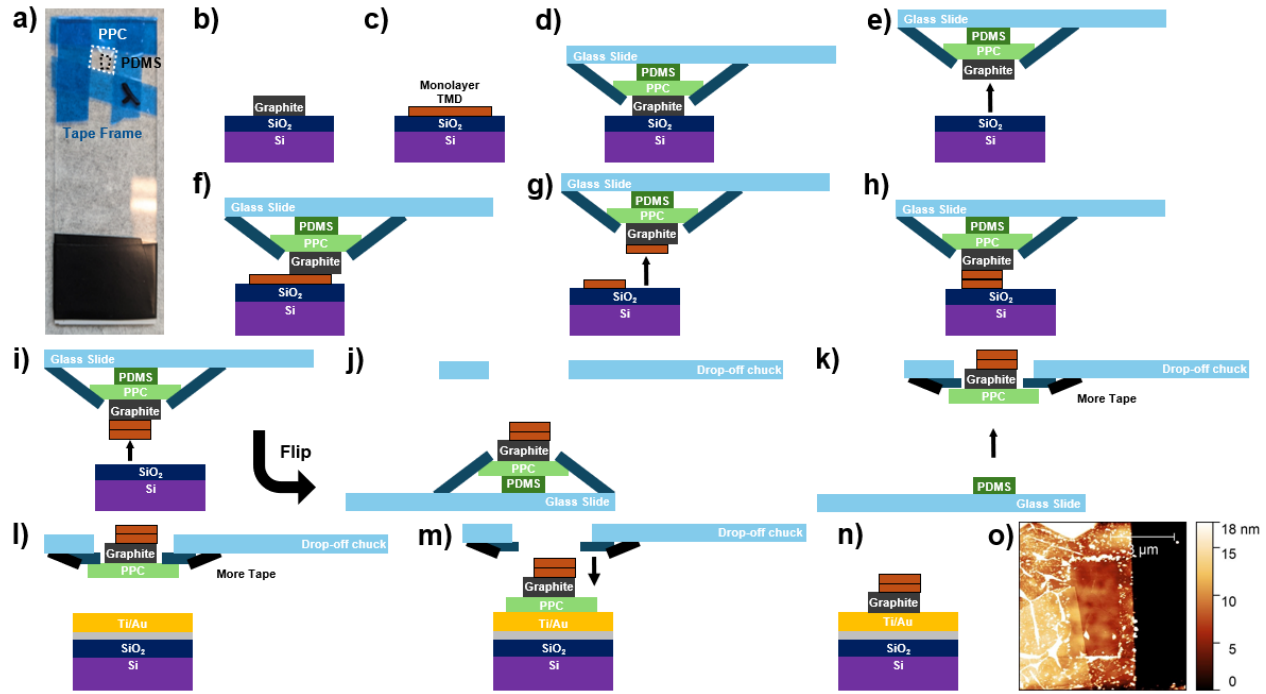


Figure 3.3: tTMD on graphite sample fabrication. **(a)** PPC/PDMS stamp assembly. **(b)** Schematic of bulk graphite on Si/SiO₂ substrate. **(c)** Monolayer TMD on Si/SiO₂ substrate. **(d-e)** bulk graphite picked up by PPC/PDMS stamp. **(f)** Contacting first half of TMD with graphite, **(g)** picking up first half of TMD **(h-i)** Picking up the other half of TMD after introducing twist **(j)** inverting 2D material stack and **(k)** transferring 2D material stack to transfer chuck **(l-m)** dropping off sample on substrate **(n)** clean sample **(o)** AFM image following AFM cleaning of the region.

To pick up the first layer of TMD, the TMD monolayer substrate is placed on the transfer station stage and heated to 40°C. The TMD is then aligned with the graphite on the stamp. The stamp is then slowly approached, with the contact "fringe" moving across the sample, until the graphite is brought into contact with the first half of the TMD flake, while leaving the second half untouched (Figure 3.3(f)). The graphite and TMD are held in contact for approximately one minute. The stamp is then quickly raised, peeling off the first half of the TMD flake (Figure 3.3(g)). The desired twist is then introduced, and the process is repeated to pick up the other half of the TMD flake (Figure 3.3(h-i)).

Inversion and drop-off

The 2D material stack must then be deposited on a Au-coated substrate. A SiO_2/Si substrate is coated using PVD with 5nm Ti (adhesion layer) and 50nm Au. The 2D material stack must be deposited TMD-side up; oriented opposite from how it was assembled. It is therefore necessary to deposit the stack inverted. This is accomplished through the use of a "transfer chuck" which consists of a glass slide with a 10mm diameter circular hole in one end.

The tape frame and PPC film bearing the vdWH are peeled off of the slide, leaving the PDMS behind. They are affixed using additional tape to the underside of the transfer chuck, with the 2D material stack TMD side up under the hole (Figure 3.3(j-k)). The transfer chuck and substrate are then mounted in the transfer station. The transfer chuck is approached to within $\sim 5\text{mm}$ of the substrate, which is heated to 60°C , relaxing the PPC film without melting it (Figure 3.3(l)). The stack is then aligned with a clean region near the center of the substrate and slowly approached until it makes contact. The stage is then heated to 150°C to induce a glass phase transition, melting the PPC (Figure 3.3(m)). The transfer chuck can then be lifted and removed. The substrate is left at temperature for ten minutes to ensure the PPC film adheres.

Cleaning

While the method described in Section 3.2.1 ensures the cleanliness of the TMD-TMD interface, it does leave a significant amount of polymer on the surface which must be removed (Figure 3.3(n)). This is accomplished through a series of annealing and mechanical cleaning steps. The sample is first annealed in 19:1 Ar:H gas for 10 hours at 230°C . This step is to remove as much polymer as possible to maintain the cleanliness of the vacuum furnace used in the next step. The sample is then vacuum-annealed for one hour at 300°C .

After annealing, the sample undergoes AFM cleaning, in which it is repeatedly scanned in contact with a low spring-constant cantilevered tip. If the tip-sample force is chosen appropriately, the tip will sweep contaminants off the surface without damaging the sample (Figure 3.3(o)). The AFM cleaning uses a force of 350 nN , scanning at a resolution of approximately 50 lines per μm . The scan direction is then rotated 90° and the process is repeated. After AFM cleaning, a detailed semi-contact AFM image is taken to map the sample surface. This map will facilitate navigation in the STM. Now clean, the sample is mounted on a flag-style sample plate using conductive H21D silver epoxy, and loaded in the STM where it can be measured.

3.2.2 Challenges

The method described in Section 3.2.1 does not produce a pristine surface, but rather surfaces that feature cracks, bubbles, and areas of delamination, as shown in Figure 3.4(a). This may be due to the violent nature of the "tear" in the tear-and-stack process. While these features can be useful for navigating on the sample surface, they also lead to twist angle disorder, with variation of as much as 3° from the engineered twist angles. While the local twist angle can vary gradually due to strain, as shown in Chapter 4, more typically, a region of roughly uniform twist is interrupted by cracks or linear bubbles, across which the twist angle can be significantly different. This is illustrated in Figure 3.4(b), which consists of an STM topography map from a twisted multilayer graphene sample, but illustrates the same phenomenon present in TMDs. The moiré period changes significantly across a linear discontinuity due to a change in interlayer twist. Twist angle variation within a sample can be an advantage, as it allows for the study of multiple regimes in one device. However, if more precise control is desirable, it may be necessary to employ less violent techniques to tear the TMD. Techniques exist to cut the flake in half before picking it up to reduce this disorder, including cutting with an STM or contact mode AFM, [94, 141] plasma

etching, [142] or laser cutting [143], and could be applied in future work.

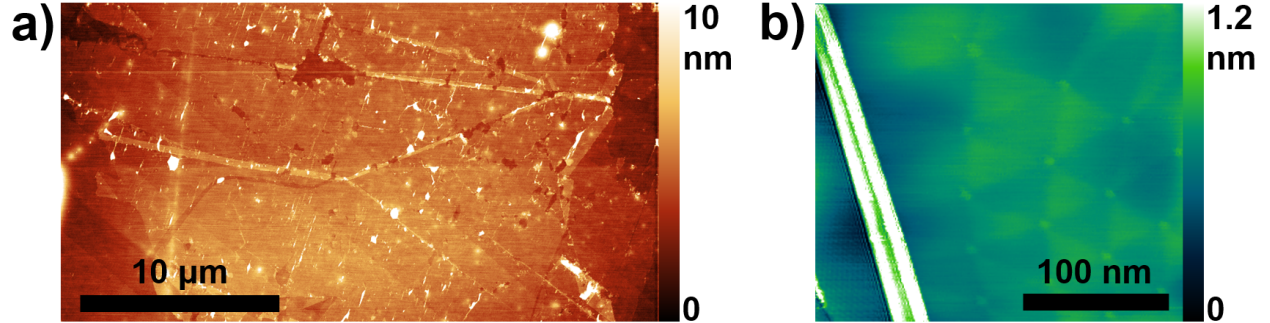


Figure 3.4: Challenges with tTMD sample fabrication. **(a)** AFM images of typical tTMD sample surface, showing cracks, bubbles, and folds. **(b)** STM topography image of twisted multilayer graphene, showing twist angle change resulting in the change of moiré period across a linear bubble.

3.3 Continuing development: electrostatic doping

As discussed in Chapter 1, twisted bilayers of TMDs are of interest for the many-body physics they host, which lead to properties that are sensitive to filling factor. It is therefore desirable to produce STM-compatible tTMD samples with electrostatic doping capabilities, which would allow for tuning of the filling factor. This is accomplished through a back gate: a conductive layer underneath the sample which can be biased to adjust the Fermi level of the sample relative to its charge neutrality point.

Implementing a back gate presents an experimental challenge, as the graphite substrate used in the sample fabrication procedure described in Section 3.2 would screen the back gate. The tTMD must instead rest on a dielectric. A sample fabrication procedure was developed to meet this constraint while solving the conductivity problems associated with the samples presented in Section 3.1.

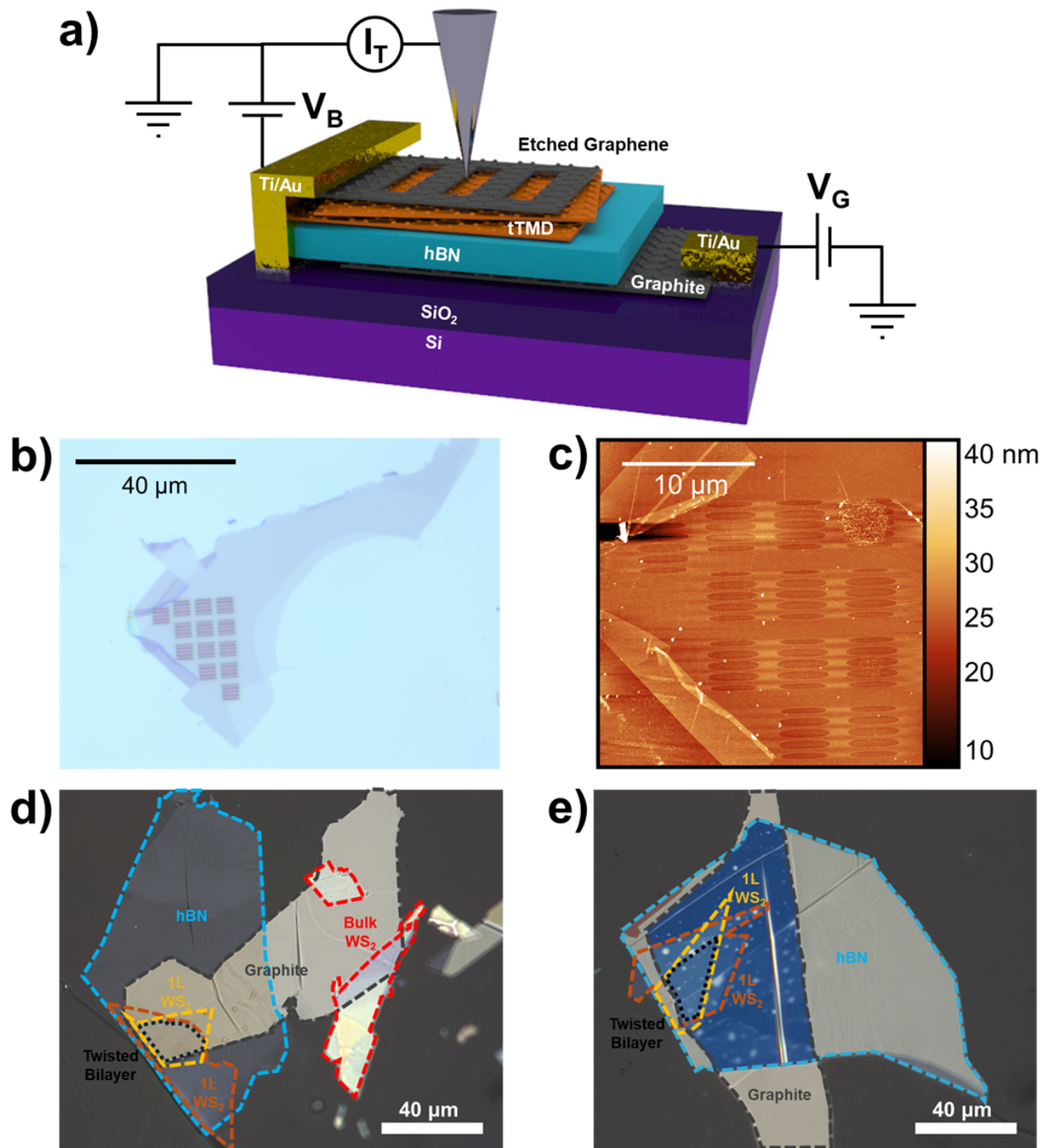


Figure 3.5: Backgated tTMD sample fabrication. **(a)** Sample schematic of back gated tTMD sample. **(b)** optical micrograph and **(c)** AFM topography of windows etched in graphene. **(d-e)** backgated sample attempts.

As shown in Figure 3.5(a), the back gated sample design consists, listing elements

from the bottom up, of the graphite backgate, the hBN dielectric, the tTMD sample, and a graphene contact, which consists of few-layer graphene patterned with "windows". The TMD can be accessed by the STM through the windows, limiting the path of charge carriers to graphene allowing for reduced in-plane resistance. The stack is assembled with the inverted transfer technique as described in Section 3.2.1 and then deposited on a SiO₂/Si substrate. Intrinsic (undoped) Si is used to prevent shorts through the substrate. The top contact and back gate are then contacted with Ti/Au contacts, patterned with electron-beam lithography, and deposited with PVD. The top contact pad is larger, giving a bigger target to land on. It is critical that the tTMD and top contact remain electrically disconnected from the back gate.

A key step in this process is the patterning of the top-contact graphene. The windows in the graphene can be patterned with electron-beam lithography and etched with reactive ion plasma etching, as shown in Figure 3.5(b-c).

First, few-layer graphene flakes are exfoliated onto Si/SiO₂ substrates and identified optically. The substrates are then coated with 950K A6 PMMA which acts as a positive resist for electron-beam lithography. The electron-beam lithography pattern consisted of a grid of $400nm$ by $4\mu m$ windows, separated by $400nm$ wide graphite ribbons, as shown in Figure 3.5(b) and (c), with a thicker ribbon every five windows to improve the structural integrity of the flake. The patterning was performed with a dose of $100C/cm^2$, and developed in 40 : 3 IPA:H₂O at room-temperature for 45s. After development, the flakes were etched with O₂ at 25Pa, 30sccm at a power of 20W. Due to over-etching or over-development, the windows produced in this example were measured with AFM to be $500nm$ wide.

The graphene window array can then be picked up as part of the inverted transfer process. Of the two samples that reached this stage, one tore the graphene during pickup, resulting in insufficient coverage of the TMD, as shown in Figure 3.5(d). The other picked

up successfully, as shown in Figure 3.5(e), but the polymer could not be cleaned off with standard methods, likely owing to contamination in the stamp-making process.

While no samples have yet been produced with the recipe presented in Section 3.3, each step has been performed successfully. Further development may be necessary to overcome the low yield of some steps, but in principle, this recipe is achievable and allows for a tTMD-based quantum simulator.

Chapter 4

In-plane reconstruction and interfacial ferroelectricity in parallel aligned transition metal dichalcogenides homobilayers

In this chapter, we will discuss the structural properties of twisted bilayer transition metal dichalcogenides (TMDs) and the emergence of interfacial ferroelectricity. We will then present scanning tunneling microscopy (STM) results on ferroelectric stacking order domains in twisted bilayer WS_2 . This chapter presents a modified version of the paper **L. Molino, L. Aggarwal, V. Enaldiev, R. Plumadore, V.I. Fal'ko, A. Luican-Mayer. "Ferroelectric switching at symmetry-broken interfaces by local control of dislocations networks". *Adv. Mater.*, 35, 38, 2207816 (2023).**

4.1 Structural relaxation

Structural relaxation is a key area of investigation in twisted TMDs [82–84, 87, 88, 91, 95, 130, 143–146]. In the process of fabricating twisted bilayers, two layers are brought together and can be thought of initially as rigid crystal lattices. However, when the two layers are in contact, different stackings across the moiré pattern have different equilibrium interlayer spacing, resulting in out-of-plane corrugation.

In the case of small angle homobilayers (typically under $\sim 2^\circ$ in parallel- (P-) aligned TMDs, $\sim 0.9^\circ$ in anti-parallel- (AP-) aligned TMDs) [130], in-plane deformation also becomes significant. High symmetry stackings in twisted TMDs have inequivalent van der Waals energies, and the lower symmetry stackings are even more unfavorable. Driven by the dependence of the bilayer energy on stacking order, long wavelength moiré patterns can undergo local dilation and rotation [95] to increase the area of the preferred stacking. This deformation is controlled by the balance between the van der Waals energy gained by increasing the area of preferred stacking, and the elastic energy cost associated with the deformation [82]. In the long-wavelength limit, regions of uniform stacking order emerge. These are called stacking order domains. The domains are bound by highly strained shear solitons, called domain walls (DWs). These DWs are now the locus of the majority of the elastic energy, which now varies with the DW length. The domain wall network (DWN) will have the same periodicity as the moiré pattern from which it arises. It is for this reason that DWNs only form in low twist-angle homobilayers; these structures have a long moiré period, and therefore form large domains with a low perimeter-to-area ratio, allowing for a favorable balance of van der Waals and elastic energy.

P- and AP- aligned bilayers both host three high symmetry stackings, which are all stable or metastable states, as shown in Figure 4.1(a) and (b). Theoretical work has been performed to characterize the van der Waals stacking energies of each of these phases [130, 142, 147, 148].

DWNs can take on a few particular forms, as shown in Figure 4.1(c). In P-aligned bilayers, the XM' and MX' are both energy minima, and therefore the DWN takes the form of alternating equilateral triangles of XM' and MX'. In the AP case, the 2H-AP and MM' stackings are nearly energetically equivalent, resulting in Reuleaux triangles, with DWs curving to increase the area of 2H-AP. The amount of DW curving is again controlled by the balance

of van der Waals and elastic energy. At very-near-zero twist-angles, the walls of Reuleaux-triangles begin to merge [83, 87, 88, 130, 148]. As the twist angle approaches zero, the MM' domain is "squeezed-out", resulting in hexagonal regions of 2H-AP, separated from each other by double DWs, with small regions of MM' in the corners [88, 130, 148].

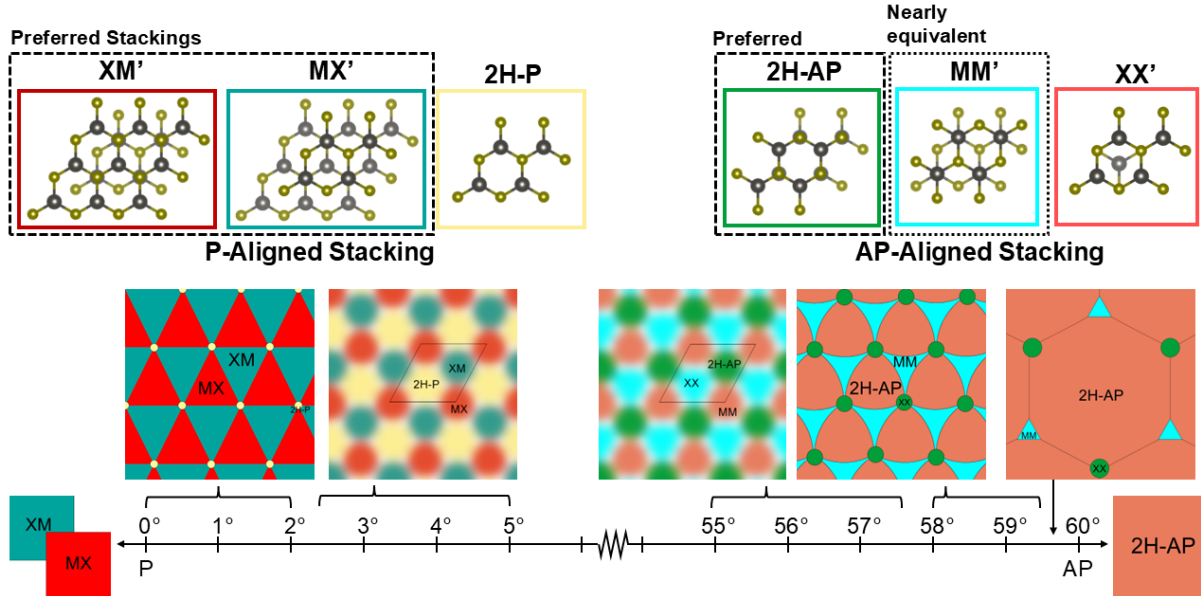


Figure 4.1: Reconstruction phenomena as a function of twist angle in twisted homobilayer TMDs.

4.2 Interfacial ferroelectricity

In P-aligned bilayers, the XM' and MX' high symmetry stackings are notable because they lack inversion symmetry. This lack of symmetry allows for a net interlayer charge transfer, which occurs between the metal and the chalcogen arranged vertically, producing a net ferroelectric dipole moment [97–101, 149]. A net dipole can only be achieved in systems lacking inversion symmetry because in symmetric cases any interlayer charge transfer will be canceled by opposite charge transfer at another site, as shown in Figure 4.2.

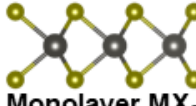
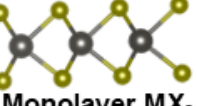
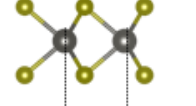
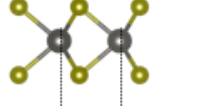
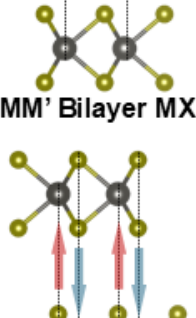
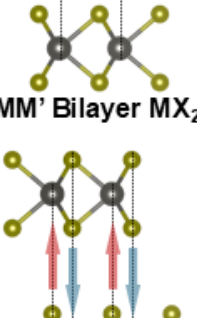
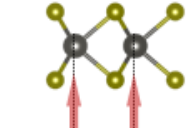
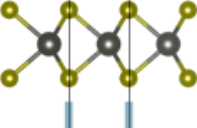
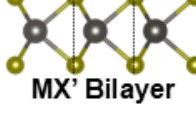
	Structure	Inverted Structure	Interfacial Ferroelectricity?
	 Monolayer MX_2	 Monolayer MX_2	 No Interlayer Charge Transfer (Only one layer)
Preferred Anti-Parallel Stackings (Inversion-Symmetric)	 MM' Bilayer MX_2	 MM' Bilayer MX_2	 No Interlayer Charge Transfer
	 2H Bilayer	 2H Bilayer	 No Net Interlayer Charge Transfer
	 MX' Bilayer	 XM' Bilayer	 Net Interlayer Charge Transfer
	 XM' Bilayer	 MX' Bilayer	 Net Interlayer Charge Transfer

Figure 4.2: Interlayer charge transfer in inversion symmetric and asymmetric TMD bilayers.

The emergence of a permanent dipole moment in two-dimensional (2D) materials is referred to as "interfacial ferroelectricity" to distinguish it from more typical ferroelectrics, and has been observed in bilayer and multilayer systems of hexagonal BN (hBN) [133, 150–154], TMDs [94, 97–101, 149, 155, 156], and is even predicted in multilayer graphene with appropriate stacking [157].

In near zero degree twisted TMD bilayers, the emergent P-aligned stacking order domain network features alternating domains of in- and out-of-plane ferroelectric dipole moment due to the opposite dipole moments of the XM' and MX' stackings. If an out-of-plane electric field is applied to these structures, the energy equivalence of adjacent domains is broken [100, 101, 143]. In this case, the DWs curve to maximize the area of preferred stacking, governed by the same balance of energy as the curving of DWs in AP-bilayers, except with the additional contribution of electric potential energy. In a typical P-aligned DWN in an out-of-plane field, the vertices are topologically protected, and effectively "pin" the DWs. Thus, at high applied fields, the unfavorable stacking can be effectively "squeezed out", through the formation of double DWs, but the periodicity of the DWN remains unchanged. However, in cases where the DWs terminate at the edge of the sample, they are free to slide in response to the field. Thus, in cases where the domains are at the scale of the sample, the stacking order of the surface can become uniform over the entire surface through this ferroelectric sliding [98, 133, 134]. In either case, the DW bending and sliding is reversible.

4.3 Ferroelectric switching at symmetry-broken interfaces by local control of dislocations networks

This section present a modified version **L. Molino, L. Aggarwal, V. Enaldiev, R. Plumadore, V.I. Fal'ko, A. Luican-Mayer. "Ferroelectric switching at symmetry-broken interfaces by local control of dislocations networks". *Adv. Mater.*, 35, 38, 2207816 (2023).** This

paper explores the very-near-zero twist regime in bilayer WS_2 via STM. It demonstrates local control of the bending of the DWs with the electric field from the tip, representing the first case of local control of the surface ferroelectric moment. This work also examines the role of anisotropic strain on the domain geometries and their response to an out-of-plane field, and develops a theoretical model for DW bending in the strained case.

The experiments in this work were suggested by Adina Luican-Mayer (A.L.-M.). The samples were prepared by Laurent Molino (L.M.). The data was collected and analysed by L.M. and Leena Aggarwal (L.A.), with advice from Ryan Plumadore (R.P.), using software written by L.M.. The code used in this work is presented in Sections 8.2 and 8.3 in the Appendix. The COMSOL calculations were performed by L.M.. Vladimir Enaldiev and Vladimir I. Fal'ko provided the theoretical model and contributed to the interpretation of the data. The manuscript was drafted by L.M. and edited by all authors. In Section 4.3.11, additional work STM work from authors L.M. and L.A., preformed after the submission of **L. Molino et al. *Adv. Mater.* 35, 38, 2207816 (2023)** of is presented that investigates hysteresis.

4.3.1 Introduction

Overcoming challenges in modern computer engineering and telecommunication technologies requires compact multi-functional components. Atomically thin films of semiconducting TMDs offer multiple advantages for such a development. They retain robust semiconducting properties down to sub-nanometer thickness, which allows for an efficient transistor operation, and they exhibit strong light-matter coupling. Moreover, hBN and TMDs have recently emerged as ferroelectric 2D materials, in which switching between two twin stacking orders by mutual sliding of the layers and electrical manipulation produces room-temperature (RT) stable out-of-plane polarization [97–101, 133, 150, 153]. Semiconducting ferroelectrics with low energy barrier polarization switching are of interest, as they en-

able ferroelectric field-effect transistors, devices that combine memory storage and logic processing into a single device [149]. The possibility of assembling vertical stacks of designer sequences from atomically thin planes of layered van der Waals materials allows for unprecedented flexibility in engineering novel electronic devices [2, 3]. In particular, previously inexistent electronic properties can emerge in these systems through relative rotation of the atomically thin layers, which leads to the formation of moiré patterns and reconstruction domains [82, 148, 158].

Lack of inversion symmetry among individual monolayers of TMDs permits control over the symmetry of interfaces formed in layer-by-layer assembled heterostructures. For example, when assembling two layers with inverted orientation of unit cells, one obtains bilayers with a local inversion-symmetric structure, which reconstructs [82, 148, 159] (at small twist angles) into a honeycomb set of 2H stacking domains [130, 144, 148], separated by DWs that have the form of intra-layer shear solitons [147]. Moreover, the assembly of layers with parallel orientation of unit cells (P-bilayers) generates structures with non-symmetric interfaces that allow for a spontaneous interlayer charge transfer and, therefore, out-of-plane ferroelectric polarization [97, 98, 133, 134, 150, 153]. The bilayers with parallel orientation of monolayer unit cells exhibit two energetically equivalent favorable stacking orders, which are mirror images of each other (illustrated in Figure 4.3(a)). In one type of stacking (XM'), the metal site M' of the bottom layer appears under the chalcogen site X of the top layer, whereas the chalcogen/metal sites (X'/M) in the bottom/top layers sit under/over the middle of the honeycomb of the other layer's lattice. In the second type of stacking (MX'), the metal site M of the top layer appears over the chalcogen site X' of the bottom layer, whereas the chalcogen/metal sites (X/M') in the top/bottom layers sit over/under the middle of the honeycomb of the other layer's lattice. The distribution of transferred charge density between the layers is shown in Figure 4.3(a), for XM' stacked WS_2 bilayers (see

Section 4.3.13) for details on the calculation). This demonstrates formation of an electrical dipole layer between the inner chalcogen sublayers, that is characterized by electric polarization areal density $P = 3.2610^{-3}e/nm$, suggesting that this system features an interfacial ferroelectric effect.

For small-angle twisted P-bilayers, in-plane relaxation [82, 130, 144, 148] leads to the alternating twinning of XM' and MX' domains carrying opposite electric polarization [130, 134, 144, 148, 160]. These domains are separated by DWs that are similar to partial dislocations in the 3R polytype of bulk TMDs. In the context of the interfacial ferroelectric effect, by coupling the domain polarization to an out-of-plane electric field, it should be possible to change the polarization of the sample by domain switching, which involves structural changes. In the context of the interfacial ferroelectric effect in twistrionic structures this appears as a lateral interlayer shift of the lattices transforming MX' into XM' stacking (or vice versa, depending on the direction of the out-of-plane electric field). This repolarization via structural modification happens primarily at the boundaries of domains with the opposite polarization, leading to the shift in the DW position (as it also happens in bulk ferroelectrics).

4.3.2 Scanning tunneling microscopy observation of domain wall network

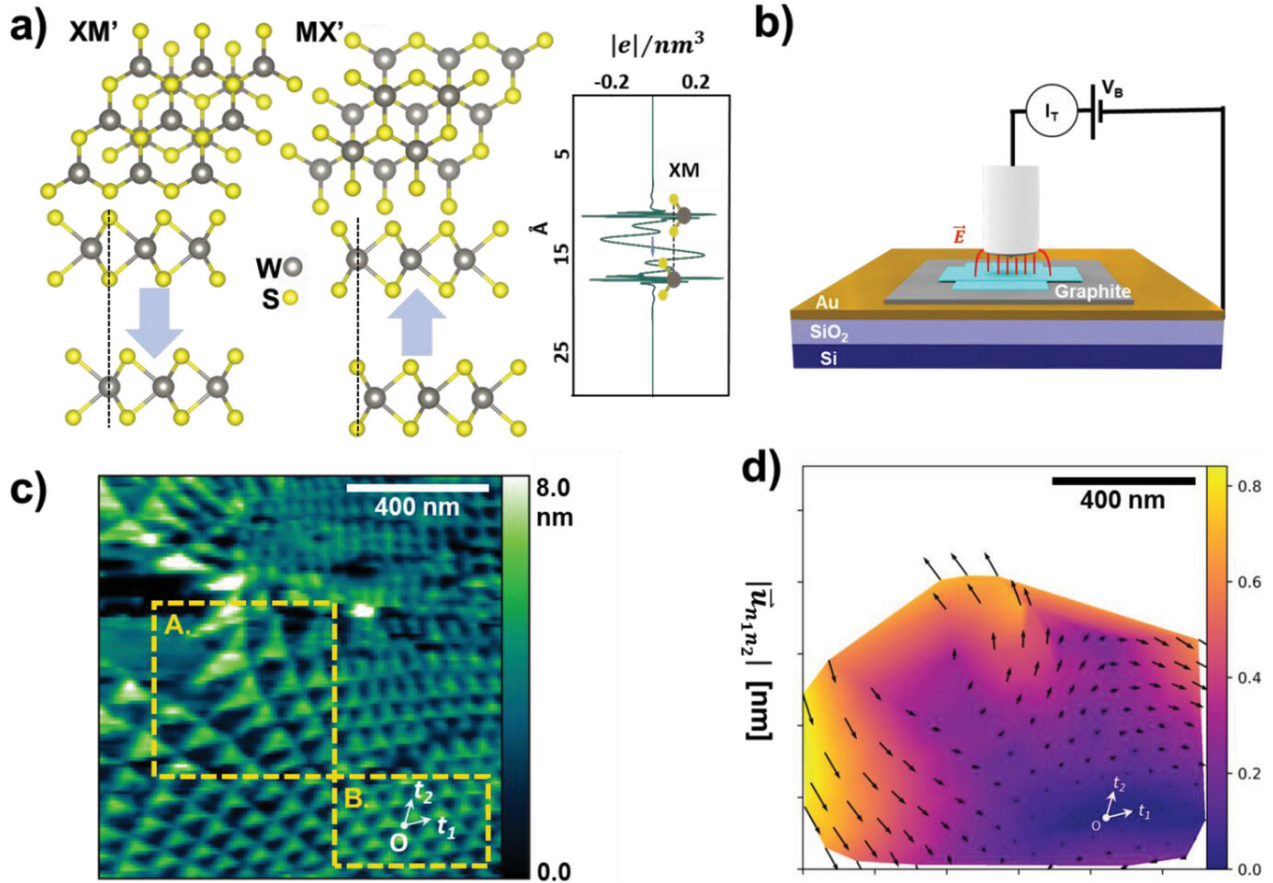


Figure 4.3: **(a)** Top and side views of XM' and MX' stackings, with arrows indicating the direction of electric polarization. Inset shows in-plane-averaged charge density transferred between the layers, which is equal to antisymmetric (with respect to the middle plane between the layers) part of total charge density for XM'-stacked WS₂ bilayer. **(b)** Schematic of the STM experiment, indicating the electric field produced by applying a bias voltage between the tip and the sample. **(c)** Large STM topographic map ($V_B = -1.3V$, $I_T = 50pA$), showing two distinct regions in the sample indicated by A and B. In area B, the triangular moiré superstructure is homogeneous, with equilateral triangles, and has periodicity given by the translation vectors $\vec{t}_{1,2}$. In area A, the moiré pattern is skewed due to a small strain in one of the layers (whose effect is magnified by the moiré superlattice effect [161]). **(d)** Spatial displacement field map for the inter-layer deformations, obtained using Equation 4.1 from the variation of moiré superlattice pattern in (c).

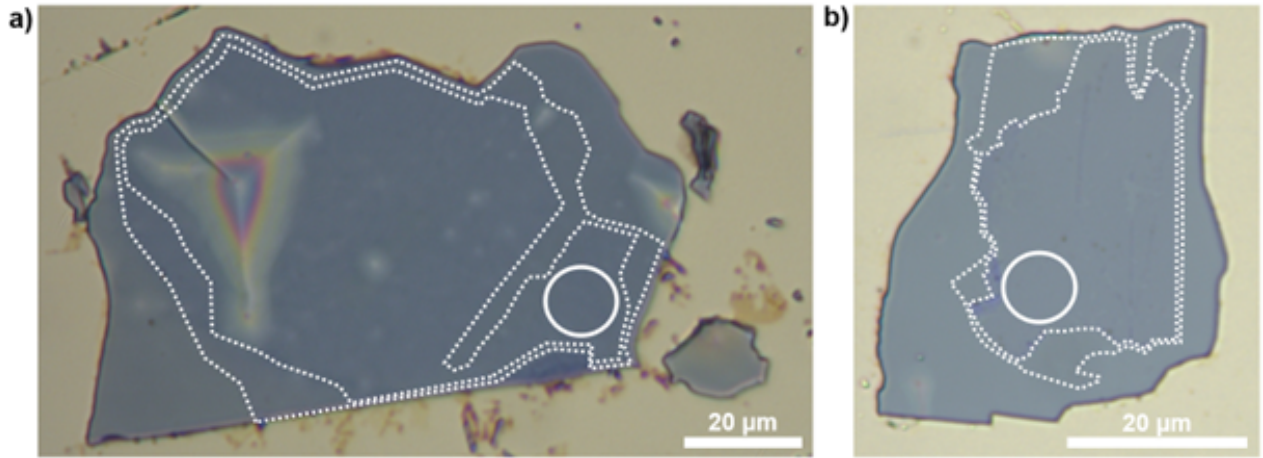


Figure 4.4: Optical micrograph of Samples 1 **(a)** and 2 **(b)**. Dotted lines indicate approximate boundaries of the WS_2 layers. Circles indicate approximate area where data were collected.

Below, we study regimes and evolutions of interfacial-ferroelectric domain structures using P-aligned WS_2 samples. Those were assembled as schematically indicated in Figure 4.3(b) (optical micrographs are available in Figure 4.4). A thin graphite film was placed under the TMDs to improve electrical contact. Scanning tunneling microscopy (STM) and spectroscopy (STS) was used to image and control the reconstruction domains (XM' and MX') formed in the twisted WS_2 samples. As indicated in Figure 4.3(b), such an experiment implies the presence of a perpendicular electric field between the tip and the sample, which can couple to the local polarization of the XM' and MX' stacking areas. A typical scanning tunneling topography for our samples (Figure 4.3(c)) shows large triangular domains of XM' and MX' stacking (Figure 4.3(a)), separated by a network of DWs with clearly identifiable nodes (to which one can attribute [148] energetically unfavorable XX' stacking characterized by vertical alignment of chalcogens in the top and bottom layers). According to the earlier observations [130, 134, 144] and theories [148], such domains form in P-aligned bilayers of TMDs for the twist angles below 2.5° . We note that, as such images are acquired in constant current mode, the large apparent height misrepresents the actual

topography of the sample surface (in particular, reflecting the effect of electric polarization on the value of tunneling current from the tip into the substrate).

In Figure 4.5, STM topography maps are presented showing atomic resolution on the MX' and XM' domains.

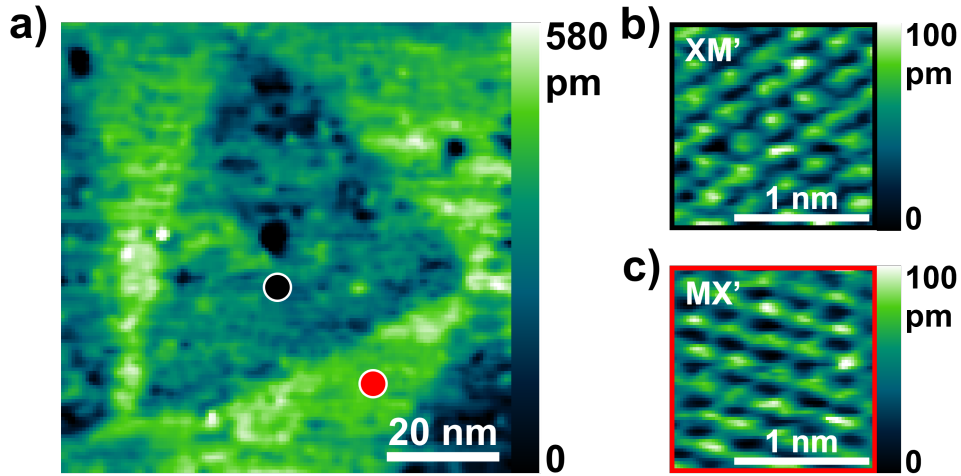


Figure 4.5: Atomic resolution STM topography on WS_2 bilayer. **(a)** XM' and MX' stacking order domains with approximate sites of atomic resolution measurements of **(b)** and **(c)** indicated by black and red circles. **(b)** Atomic resolution on XM' and **(c)** MX' domains. Lattice constants were measured to be $2.8 \text{ \AA} \pm 0.3 \text{ \AA}$ in both sites ($I_T = 100 \text{ pA}$ and $V_B = -1.3 \text{ V}$).

Tip-dependent apparent height

Differences in the surface density of states between the XM' and MX' stacking order domains lead to a difference in their apparent height in an STM image. In Figure 4.6 we plot the various apparent heights that we observed in 3 different samples, on 5 different areas and with 3 different tips as noted.

The most common apparent height was below $1 - 2 \text{ nm}$, in agreement with other works on similar systems. We note that among these similar data sets, Sample 1, with Tip 1, presented a larger apparent height. We attribute these variations to individually distinct macroscopic tip shapes that result in distinct electric field profile.

Importantly, the magnitude of the apparent height does not play a role in the main observation of this experiment, namely the DW curvature geometry relationship to the tip bias.

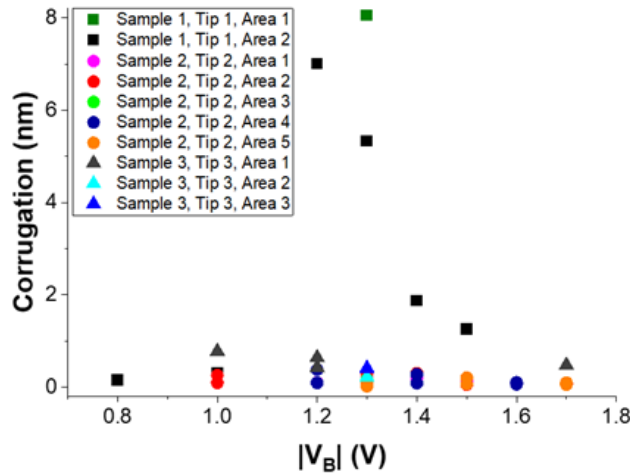


Figure 4.6: Apparent height observed in STM topography of triangular domains. Shapes indicate different tips and samples; colours indicate different areas.

4.3.3 Interlayer displacement and anisotropic strain

Within the triangular domains of the network in Figure 4.3(c), we first focus on the area B containing a network of approximately equilateral triangular domains. These equilateral domains have periodicity of $\approx 78\text{nm}$ corresponding [77, 130, 134, 144] to a twist angle 0.23° . This area will be used as a reference for the analysis of a larger-scale aperiodic domain pattern (domains of various sizes and with pronounced anisotropy). Such a distortion of the domain network is caused by a small accidental strain in either of the assembled WS_2 monolayers, inflicted in the fabrication process [162]. Theoretically, it has been demonstrated [161] that a moiré pattern acts as a magnifying glass for small deformations in the constituent monolayers of the bilayer. Strain-induced shifts of the atomic registry between the layer – even as small as a fraction of the lattice constant – lead to a shift of the equivalent stacking areas in the moiré pattern by distances comparable to

the moiré superlattice period. Here, we use this generic property of moiré patterns to map the displacement field distribution (due to the accidental strain) and analyze the position of DWN nodes, which feature XX' stacking. For this, we successively enumerate all nodes by integers (n_1, n_2) , starting from the referenced point $O = (0, 0)$ inside area B in Figure 4.3(c) with approximately equilateral domains. For this area, we determine a twist angle $\theta = \frac{|\vec{a}_1|}{|\vec{t}_1|} \approx 0.0041 (\approx 0.23^\circ)$ from the moiré period, $\vec{t}_1$ in area B ($|\vec{t}_{1,2}| \approx 78nm$ and $|\vec{a}_{1,2}| = 0.315nm$). Then, we take into account that, without strain, the positions, $\vec{r}_{n_1, n_2}$, of the XX' network nodes in the rest of the sample would correspond to the mutual shift of atomic registry such that $n_1 \vec{a}_1 + n_2 \vec{a}_2 = \theta \hat{z} \times \vec{r}_{n_1, n_2}$, whereas the difference between the actual, $\vec{R}_{n_1, n_2}$, and expected, $\vec{r}_{n_1, n_2}$, positions of the network sites enables us to determine the strain-induced interlayer shift (superimposed onto the local lattice reconstruction into domains) of the monolayer WS_2 lattices as [161],

The resulting deformations map is shown in Figure 4.3(d), indicating a vortex in top left corner and discernible deformations from the sides of the analyzed area. To further elaborate the character of the moiré periodicity distortion caused by the deformations we analyzed distribution of two independent, hydrostatic and shear, strain components calculated in local principal axes. We found that the deformations produce both the hydrostatic and shear strains (Figure 4.7) that, as expected from the deformation map, attain the highest values in the vicinity of top left corner in area A in Figure 4.3(c).

Computation of displacements and strain components

To obtain map of displacements presented in Figure 4.3(d), we identified nodes of the DWN and label them successively by pair of integers, see Figure 4.18(a), with origin in the point O . Vectors $\vec{t}_1$ and $\vec{t}_2$ (60° rotated $\vec{t}_1$) form basis of moiré superlattice in area with equilateral domains determining armchair axes in the layers and twist angle $\theta = |\vec{a}_1|/|\vec{t}_1|$. As it was

explained above, displacement at node position $\vec{R}_{n_1, n_2}$ is expressed as follows:

$$\vec{u}(\vec{R}_{n_1, n_2}) = \theta \hat{z} \times \vec{R}_{n_1, n_2} - n_1 \vec{a}_1 - n_2 \vec{a}_2 \quad (4.1)$$

where primary lattice vectors of WS_2 monolayer are orthogonal to the superlattice vectors, $\vec{a}_{1,2} = \theta [\hat{z} \times \vec{t}_{1,2,3}]$.

Having determined displacement field, we compute strain tensor components for each triangle spanned by three nodes (n_1, n_2) , $(n_1 + 1, n_2)$, $(n_1, n_2 + 1)$ using first order Taylor expansion of the displacements $\vec{u}(\vec{R}_{n_1+1, n_2})$ and $\vec{u}(\vec{R}_{n_1, n_2+1})$:

$$\begin{cases} \vec{u}(\vec{R}_{n_1+1, n_2}) - \vec{u}(\vec{R}_{n_1, n_2}) = (\vec{R}_{n_1+1, n_2} - \vec{R}_{n_1, n_2}) \cdot \left(\frac{\partial \vec{u}}{\partial x} \Big|_{\vec{R}_{n_1, n_2}}, \frac{\partial \vec{u}}{\partial y} \Big|_{\vec{R}_{n_1, n_2}} \right) \\ \vec{u}(\vec{R}_{n_1, n_2+1}) - \vec{u}(\vec{R}_{n_1, n_2}) = (\vec{R}_{n_1, n_2+1} - \vec{R}_{n_1, n_2}) \cdot \left(\frac{\partial \vec{u}}{\partial x} \Big|_{\vec{R}_{n_1, n_2}}, \frac{\partial \vec{u}}{\partial y} \Big|_{\vec{R}_{n_1, n_2}} \right) \end{cases} \quad (4.2)$$

Then, we diagonalise local strain tensor $u_{ij}|_{\vec{R}_{n_1, n_2}} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \Big|_{\vec{R}_{n_1, n_2}}$ making appropriate rotation $C(\alpha)$, by angle $\alpha = \frac{1}{2} \arctan \left(\frac{2u_{xy}}{u_{xx} - u_{yy}} \right)$. In the rotated frame strain tensor $\tilde{u}_{ij}|_{\vec{R}_{n_1, n_2}} = C^{-1}(\alpha) u_{ij}|_{\vec{R}_{n_1, n_2}}$. $C(\alpha) = \text{diag}(u_h + u_s, u_h - u_s)$ is diagonal and characterised by hydrostatic, $u_h = \frac{u_{xx} + u_{yy}}{2}$, and shear, $u_s = \sqrt{\left(\frac{u_{xx} - u_{yy}}{2} \right)^2 + u_{xy}^2}$, components. In Figure 4.7(b-e) we demonstrate distributions for all extracted quantities $\vec{u}(\vec{R}_{n_1, n_2})$, $u_h(\vec{R}_{n_1, n_2})$, $u_s(\vec{R}_{n_1, n_2})$, and $\alpha(\vec{R}_{n_1, n_2})$ characterising the local deformations.

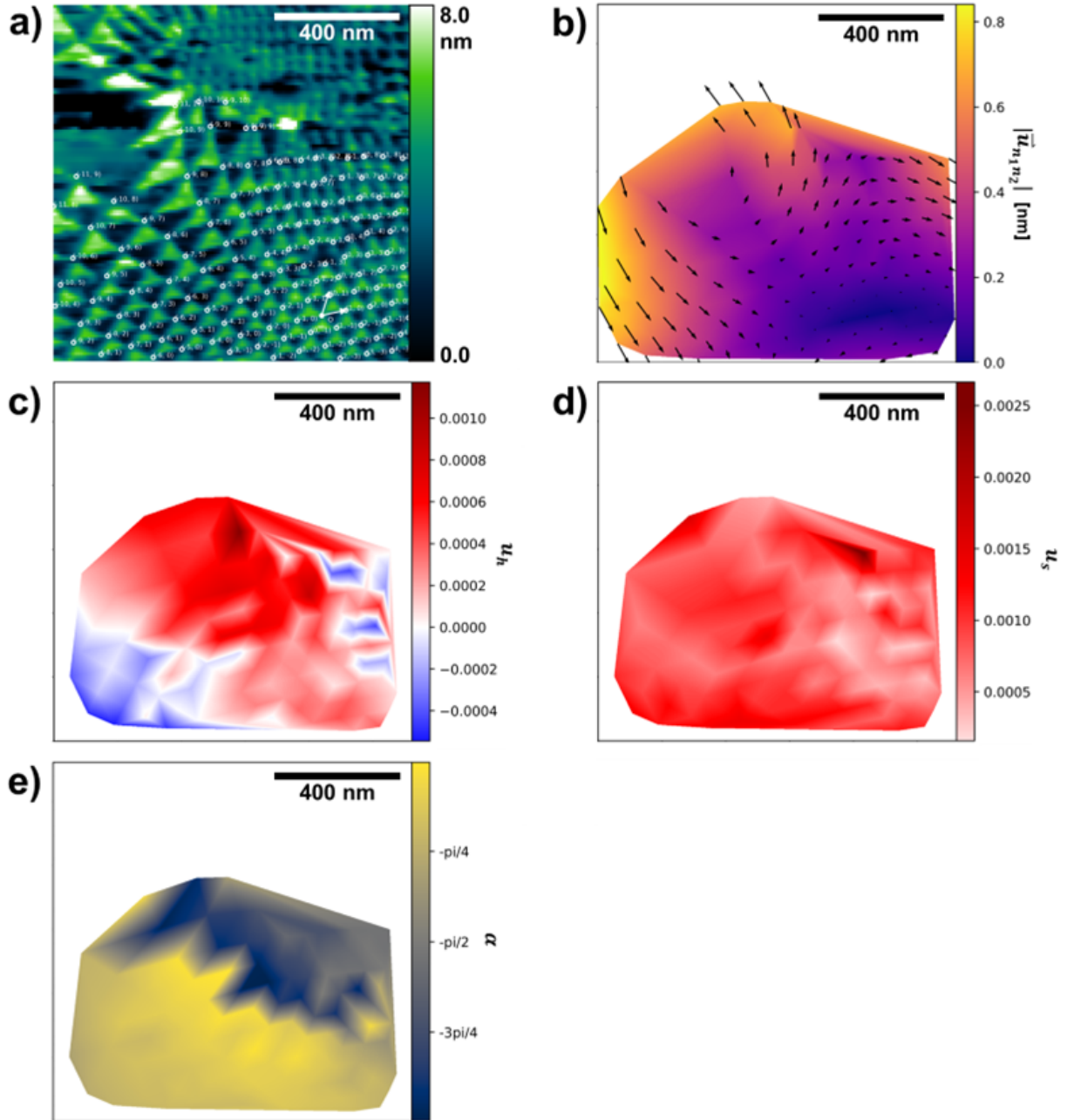


Figure 4.7: **(a)** STM topographic map ($V_B = -1.3V$, $I_T = 50pA$), with vertices label by their indices. Point O and vectors $\vec{t}_{1,2}$ are indicated. **(b)** Displacement magnitude and direction corresponding to panel (c). **(c)** Hydrostatic strain. **(d)** Shear strain. **(e)** Rotation angle α .

4.3.4 Reconstruction domain electronic properties

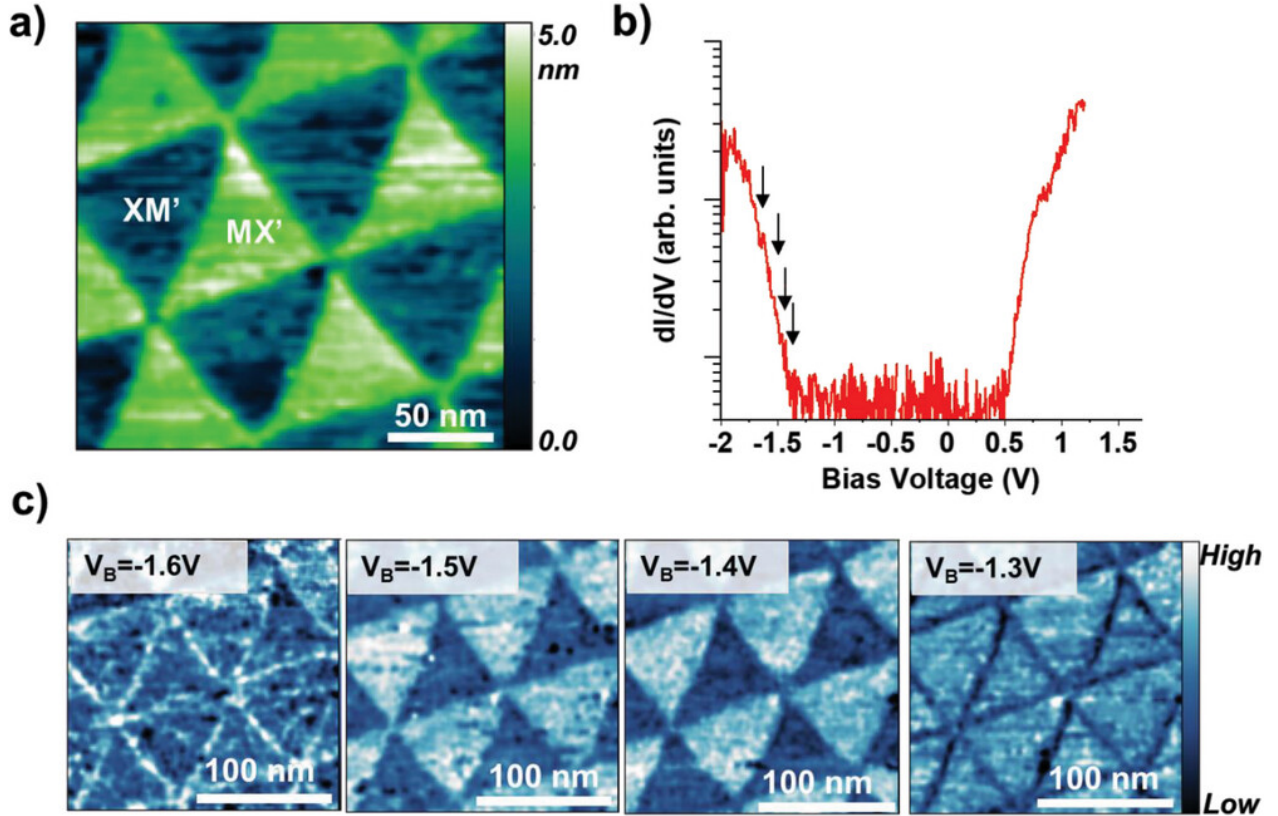


Figure 4.8: **(a)** STM topographic map of a typical region with equilateral triangular stacking order domains ($I_T = 100pA$, $V_B = -1.3V$). **(b)** STS averaged over bright and dark domains (set point: $I_T = 60pA$ and $V_B = -1.9V$). The arrows represent energies at which the data in (c) was collected. **(c)** dI/dV maps at the indicated bias voltages ($I_T = 100pA$).

The effect of the reconstruction domains on the local electronic properties, as measured using STM/STS, is discussed in Figure 4.8. The STM topographic map in Figure 4.8(a) shows a typical region with triangular domains. By observing the DW bending (domain expansion/shrinking) in response to the applied biased voltage, the bright and dark domains were identified from the ferroelectric polarization as MX' and XM' stacking regions, respectively [163]. The contrast in the STM topography of the two stackings is consistent with previously reported STM measurements of twisted TMD homobilayers with similar scan-

ning parameters [86]. The tunneling spectrum in Figure 4.8(b), averaged over all domains, shows the conduction and valence band edges at ≈ 0.6 and -1.5eV respectively, indicating an electronic band gap consistent with previous measurements of this system [164]. The differential tunneling conductance (dI/dV) maps acquired at the indicated voltages in Figure 4.8(c), demonstrate the dependence of the local density of states on the stacking order inside the domains and at the DWs. A RT comparison of MX' and XM' domain spectra is presented in Figure 4.9.

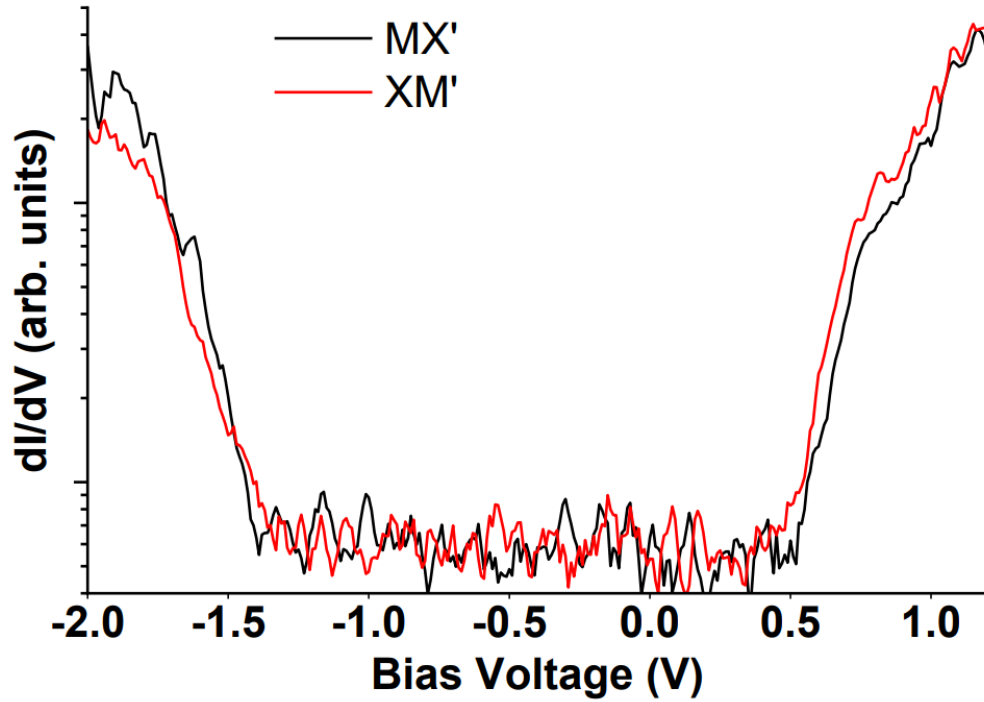


Figure 4.9: STS corresponding to Figure 4.8(b) for the MX' and XM' domains.

4.3.5 Tip-induced electric field

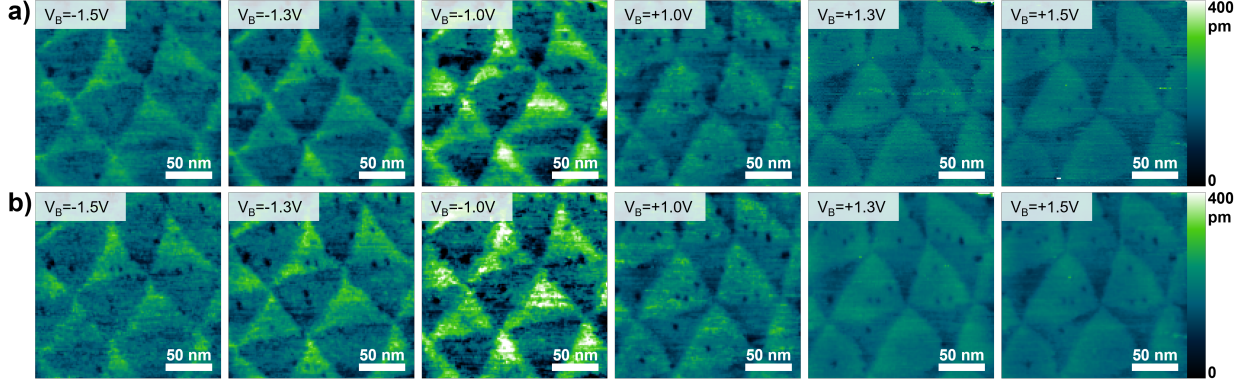


Figure 4.10: STM topographic maps in forward **(a)** and reverse **(b)** scanning directions. Data acquired at $I_T = 100\text{pA}$ and indicated biases.

Although a STM uses an atomically sharp tip end as a local probe, the overall shape of the tip and its holder make the electric field between the tip and the sample approximately uniform over a typical domain size (Figure 4.3(b)). To verify this, we compared forward and reverse topographic scans (Figure 4.10) and found them to be identical, supporting the scenario of an approximately uniform out-of-plane electric field. Such a perpendicular electric field can be controlled by varying the bias voltage between the tip and the sample. A finite element simulation of the electric field under the STM tip is presented in Section 4.3.5. In this case, an out-of-plane electric field lifts the energetic equivalence of the XM' and MX' domains, expanding the areas of those that have favored direction of polarization, thus, curving the DWs [82].

Simulation of electric field created by the scanning tunneling microscope tip

To demonstrate the approximately uniform profile of the electric field between the tip and sample over moiré superlattice period ($50 - 100\text{nm}$), we modelled electrostatic potential and field in the geometry shown in Figure 4.11(a) using COMSOL package [165].

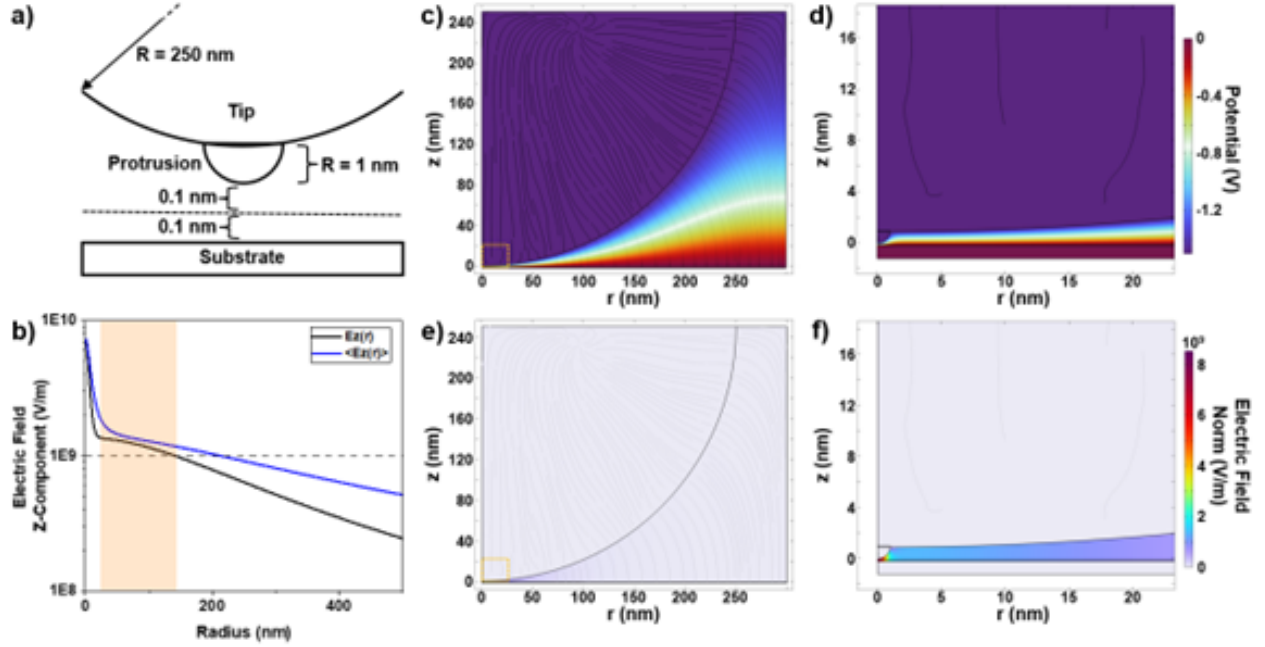


Figure 4.11: Finite element simulation of electric fields produced by a model tip geometry. **(a)** Tip geometry, not to scale. A large hemi-spherical tip with a small hemi-spherical protrusion lies above a flat substrate. The tip and substrate are assumed to be ideal conductors, and are separated by perfect vacuum. The semiconducting layer of the sample is neglected, but is assumed to lie between the tip and substrate as indicated by the dotted line. **(b)** Dependence of normal component of the electric field, $E_z(r)$ (black) and its averaged value, $\langle E_z(r) \rangle$ (blue), over a disk of radius r , centered at the tip position, at the bilayer surface (dotted line in (a)). The order of magnitude of the field necessary to observe DW bending is indicated by the dotted line. Orange rectangle indicates spatial interval with quasi-homogeneous electric field. **(c)** Map of electric potential for the entire geometry, with a $-1.5V$ potential applied between the tip and the substrate. **(d)** Same as (c) in vicinity of protrusion, shown by dotted rectangle in (c). **(e),(f)** Maps of electric field magnitude for the same regions as in (c) and (d).

Here, the tip has hemi-spherical shape, with radius $250nm$, and additional small hemi-spherical protrusion of $1nm$ radius at the end. Applying a voltage to the tip, the protrusion creates a strong electric field in its vicinity ($\lesssim 1nm$), determining the length scale at which the tunneling current occurs, responsible for the high resolution of the measured maps. The rest of the tip body produces a distribution of the electric field at the moiré superlattice scale (see Figure 4.11(c-f)). In particular, the dependence of the normal component

of electric field vs. distance from the tip center, r , at the plane of bilayer sample (Figure 4.11(b)) demonstrates that in the broad interval, $1nm \ll r \lesssim 250nm$ it varies slowly and, therefore, can be treated as quasi-homogeneous. This justifies the assumption of homogeneous electric field in our theoretical model used for description of DW bending and merging, presented below.

4.3.6 Electric field induced domain wall bending in equilateral domains

In Figure 4.12(a) we experimentally demonstrate that for a sufficiently large bias voltage, reversing the direction of the perpendicular electric field resulted in significant shape changes of the DWs, while the nodes of the domains remained in the same position. This is due to the topological nature of DWs, which precludes nucleation of new domains, with the node density determined by the local twist angle. All changes in the domain pattern are produced by the displacements of existing DWs [134], whose ends remain pinned to the nodes of the initial DWN. In the data presented in Figure 4.12(a) we find that the brighter domains tend to shrink for the negative bias voltage at the expense of the darker domains; in contrast, for a positive bias voltage, the darker domains shrink at the expense of the brighter domains, who tend to enlarge. We quantitatively analyze the shapes of such equilateral triangular domains using a previously developed model [100] for the calibration of the electric displacement field between tip and sample to the applied bias voltage. We will subsequently use the resulting calibration to capture the behavior of domain redistribution by vertical electric field across a complex network of elongated domains (e.g., in area A of Figure 4.3(c)).

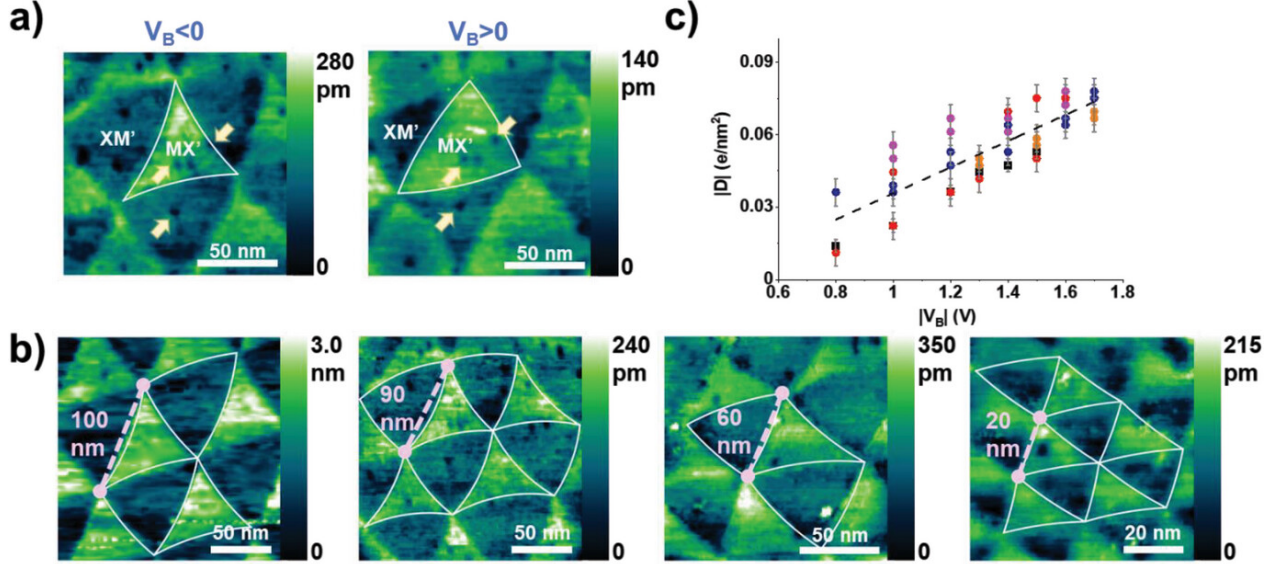


Figure 4.12: **(a)** STM topographic maps acquired at $I_T = 100pA$ and $V_B = \pm 1.3V$. The white lines represent fits with string-like model using as parameter the electric displacement field values $D = -0.075e/nm^2, 0.050e/nm^2$. We note the presence of defects (indicated by arrows), which served as a marker for the areas of interest [166, 167]. The DW dynamics were realized in an imperfect crystal, where the DWs were not pinned by defects, and where defects did not act as nucleation sites. In addition, the defects were found to be stable, even when crossed by a moving DW. **(b)** STM topographic maps of different areas with domains of indicated lengths ($I_T = 100pA$ and $V_B = -1.4V$). The white lines represent fits with the equilateral triangle DW model (from left to right: $D = -0.047, -0.070, -0.053, -0.08e/nm^2$). **(c)** The electric displacement field as a function of bias voltage for five areas, shown in 4.13. Colors indicate different areas, squares correspond to Sample 1, Tip 1, circles correspond to Sample 2, Tip 2 (Figures 4.4, 4.6).

For the equilateral domains, experimentally accessible electric fields lead only to a small bending of the DWs (partial dislocations) with ends clamped at the DWN nodes. To analyze this behavior, we used a previously developed analytical model [98, 100] predicting shape of equilateral DWs for a given field value based on an energy functional capturing the trade-off between energy costs on DW bending and energy gain, arising due to area expansion of preferentially polarized domains. The latter is provided by coupling of the ferroelectric polarization, $P = \varepsilon_0 \Delta$ (parametrised using the potential drop across the resulting double-charge layer) with electric field (parametrised using the displacement field

controlled by external charges), $-2PE = -2D\Delta$. This considers gain in energy due to growth of domain area with preferential orientation of out-of-plane D (see Equation 4.4 in Section 4.3.9). The resulting shape of each DW can be described by its transverse deflection, $y(x) = \int_0^x \frac{f(x')}{\sqrt{1-f^2(x')}} dx'$, from a straight line, $0 \leq x \leq \ell$, connecting a pair of consecutive nodes. In this expression, the function $f(x')$ is a root of a cubic polynomial, $f^3 - Af - B(x - \frac{\ell}{2}) = 0$ where $A = \frac{w}{\tilde{w}} + 2 \approx 3.52$, with $w = 1.05 \text{ eV nm}^{-1}$ characterizing minimal single DW energy per its unit length (realized for armchair direction in WS_2) and $\tilde{w} = 0.69 \text{ eV nm}^{-1}$ taking into account orientation-dependent parts (energy of partial dislocations is maximal for zigzag direction). The value of electric displacement field, D , is incorporated into another parameter in the solution, $B = \frac{2DP}{\varepsilon_0 \tilde{w}}$, which determine coupling of the field to areal density of ferroelectric polarization P in XM' (MX') domains shown in Figure 4.3(a).

Using this model, we analyzed STM topographic maps (e.g., such as in area B in Figure 4.3(b) that showed almost equilateral triangular domains at different voltages and at different length scales. By adjusting the value of the electric displacement field D for each analyzed DW, we obtained the curves represented by white lines in Figure 4.12(a) and (b). We note that this model adequately captures the shape of domain bending at different electric fields (positive and negative) as well as at different lengths between the nodes of the network. Figure 4.12(c) summarizes the values obtained for the electric displacement field as a function of bias voltage by performing such fits of DW shape for five areas on two different samples and with two different tips. The relationship (see Figure 4.12(c) between the bias voltage V_B and the electric displacement field, $D = \frac{\varepsilon_0 V_B}{d^*}$, gives us an effective distance, $d^* = 1.0 \pm 0.7 \text{ nm}$, between the tip and the sample, which is close to a typical tip-sample separation in the reported STM experiment.

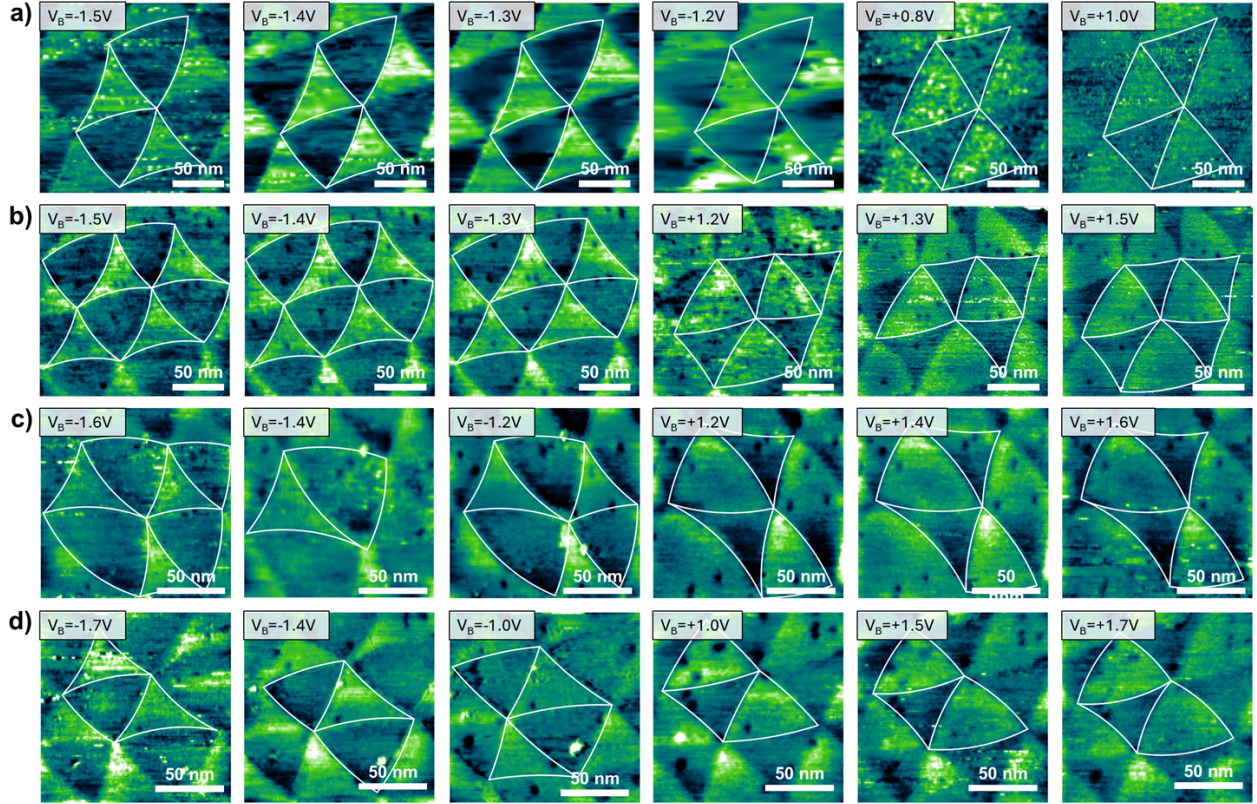


Figure 4.13: STM topography and DW fits. Data collected with Sample 1, Tip 1 **(a)**, and Sample 2, Tip 2 **(b-d)**. Panels (a–d) each represent a distinct area of the sample. Data acquired at $I_T = 100\text{pA}$ and indicated biases.

We note that the experimentally observed trend of the domain curvature increasing with the domain size ℓ is also a way to rule out electrostriction as a possible mechanism for the observed phenomena. Electrostriction is the physical deformation of a dielectric or semi-conductor in response to an electric field, and in this case would refer to a continuous deformation of the entire bilayer rather than a shift in the DW dislocation. In the scenario of electrostriction, the bending of the domains would either not be dependent on the direction of the electric field (if each layer couples individually to the electric field), or it would be smaller for smaller domains (if the bilayer couples to the electric field), as we detail in Section 4.3.7.

4.3.7 Ruling out electrostriction as origin for domain bending

There are two possible ways one can implement electrostriction in the studied system.

1. In one, the out-of-plane electric field, E_z , between the tip and a gate, induces an in-plane strain, u_{ij} ($i, j = x, y$) in each layer of bilayer sample. Due to monolayer's honeycomb lattice symmetry, the lowest coupling between strain and electric fields should be quadratic: $u_{ij} = d_{ijzz}E_z^2$, so that such strain would be the same for positive and negative gate voltages, which contradicts our experimental observation, where the sign of electric field determines direction of DW bending and types of domains that are contracted/expanded.
2. In the other mechanism, E_z couples to the bilayer as a whole, where the lower symmetry of a parallel stacked bilayer allows for a linear electrostriction effect, $u_{ij} = d_{ijzz}E_z$. However, the rotational C_3 -symmetry of such stacking prescribes isotropic expansion/contraction of the bilayers unit cell, $u_{ij} \propto \delta_{ij}$, which could produce a uniform dilation/contraction of crystal lattices in MX'/XM' domains, and therefore their apparent area in the measurements. This could, indeed, induce some bending of DWs separating MX' and XM' domains, however, with a scaling of such bending with the domain size, ℓ , inconsistent with our experimental observations. That is, the DW curvature, κ , inflicted by lattice dilation/contraction would be larger for smaller domains (here we should compare an increase of area of inflating domains by $\Delta S = \kappa \ell^3$ to the expected effect of their lattice dilation, $\Delta S = d_{ijz}E_z \ell^2 \sqrt{3}/2$, hence, $\kappa \propto 1/\ell$ scaling). However, in all studied samples, we observe an exactly opposite trend: the DW bending is stronger for larger domains. Moreover, we show that, for the larger domains, partial dislocation DWs merge into perfect screw dislocations (PSDs) at lower electric fields and we demonstrate an excellent agreement between the observations

and the theoretical model based on electric field coupling to interfacial dipole.

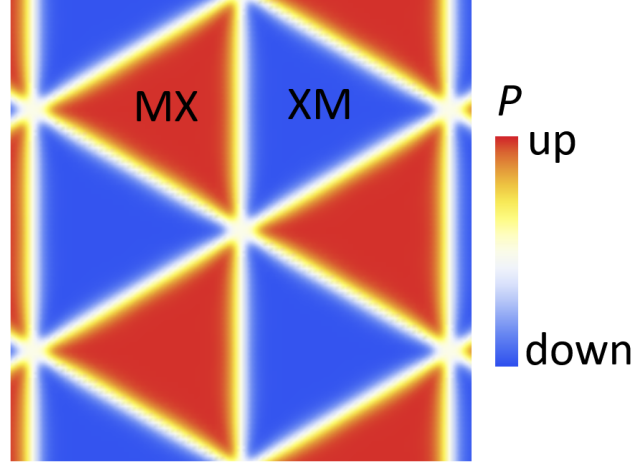


Figure 4.14: Distribution of vertical polarization across the superstructure.

4.3.8 Electric field induced domain wall bending in elongated domains

As we have pointed out in Section 4.3.3, even a small strain in one of the layers can distort the equilateral domains into elongated ones, such as those indicated in region A area of Figure 4.3(c). Examples of such measured domains are highlighted in Figure 4.15(b), where – for a strong enough electric field $D > D^*$ – the long stretches of the curved DWs (which structurally are the same as partial screw dislocations) merge together into a "full" PSDs, highlighted by red lines in Figure 4.15(b). These PSDs separate pairs of identically polarized MX' domains. Hence, we extend the domain network modelling to deformed triangular domains, where two of the inter-node distances, $\ell_{1,2}$, are longer than the third one, ℓ_3 . For the non-equilateral domains, the anisotropy of DW energy is described by $w + \tilde{w} \sin^2 (\phi_{1,2,3} + \arctan (\gamma'_{1,2,3}))$, where angles $\phi_{1,2,3}$ characterize deviations of DWs from the closest armchair direction at $D = 0$, (see Section 4.3.9), and $\arctan (\gamma'_i)$ appears due to a local transversal deflection, γ_i induced by electric field. The DW shapes are found

by minimizing the energy functional elaborated in detail in Section 4.3.9 with the following boundary conditions: $\gamma_{1,2}(\mathcal{L} \cos(\alpha_{1,2})) = \mathcal{L} \sin(\alpha_{1,2})$ and $\gamma_{1,2,3}(\ell_{1,2,3}) = \gamma_3(0) = 0$. The first of those accounts for the emergence of a PSD streak of length $\mathcal{L}$ (see Section 4.3.9), where we also define angles $\alpha_{1,2}$.

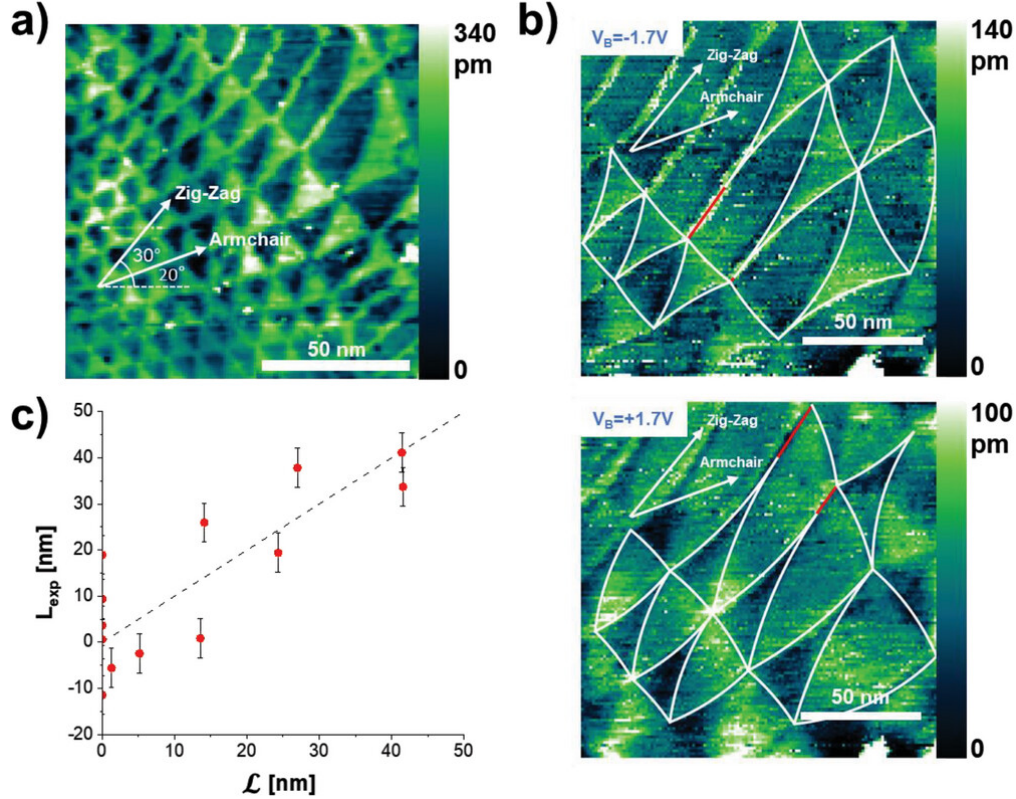


Figure 4.15: **(a)** STM topography with observed angle of armchair direction indicated. Data acquired at $V_B = -1.3V$, $I_T = 50pA$. **(b)** STM topography of a region in top-left of panel (a). Images taken at $I_T = 100pA$ and $V_B = 1.7V$. Single DW fits from string-like models plotted in white, predicted double DWs plotted in red with $A = A(\phi)$ where ϕ is the angle of the triangle side relative to the nearest armchair direction. D values of -0.067 and $0.070e/nm^2$ are used for the two images. As we already determined the effective distance that characterized the equilateral triangles (Figure 4.12), in the case of the elongated triangles, drawing the shapes of the DWs was done free of tunable parameters: the only input is the position of the network nodes. **(c)** Predicted PSD length $\mathcal{L}$ compared to observed length for elongated domains, as observed in Figure 4.16 (see Section 4.3.10 for details on estimating L_{exp}) The error bars reflect the pixel size of our images.

To find these PSD parameters, we consider that the transversal shifts γ_1 and γ_2 bring

the DW together at the PSD end, $x_{1,2} = \mathcal{L} \cos(\alpha_{1,2})$. For $\alpha_{1,2} \ll 1$, justified for the strongly elongated domains in Figure 4.15(a), the condition can be approximated by,

$$\mathcal{L} = \frac{\ell_1 - \sqrt{\ell_1 \frac{2A_1}{B} \tan(\alpha_1)}}{\cos(\alpha_1)} = \frac{\ell_2 - \sqrt{\ell_2 \frac{2A_2}{B} \tan(\alpha_2)}}{\cos(\alpha_2)}, \quad (4.3)$$

$$\alpha_1 + \alpha_2 = \arccos\left(\frac{\ell_1^2 + \ell_2^2 - \ell_3^2}{2\ell_1\ell_2}\right),$$

where $A_{1,2} = A - 3 \sin^2 \phi_{1,2}$. Equations 4.3 enable us to describe all the details of the field-induced changes of the DWN, as marked on the maps in Figure 4.15. For a quantitative comparison, in Figure 4.15(c) we compare the theoretically computed lengths $\mathcal{L}$ of the PSD streaks with the measured values L_{exp} for different domains and electric fields.

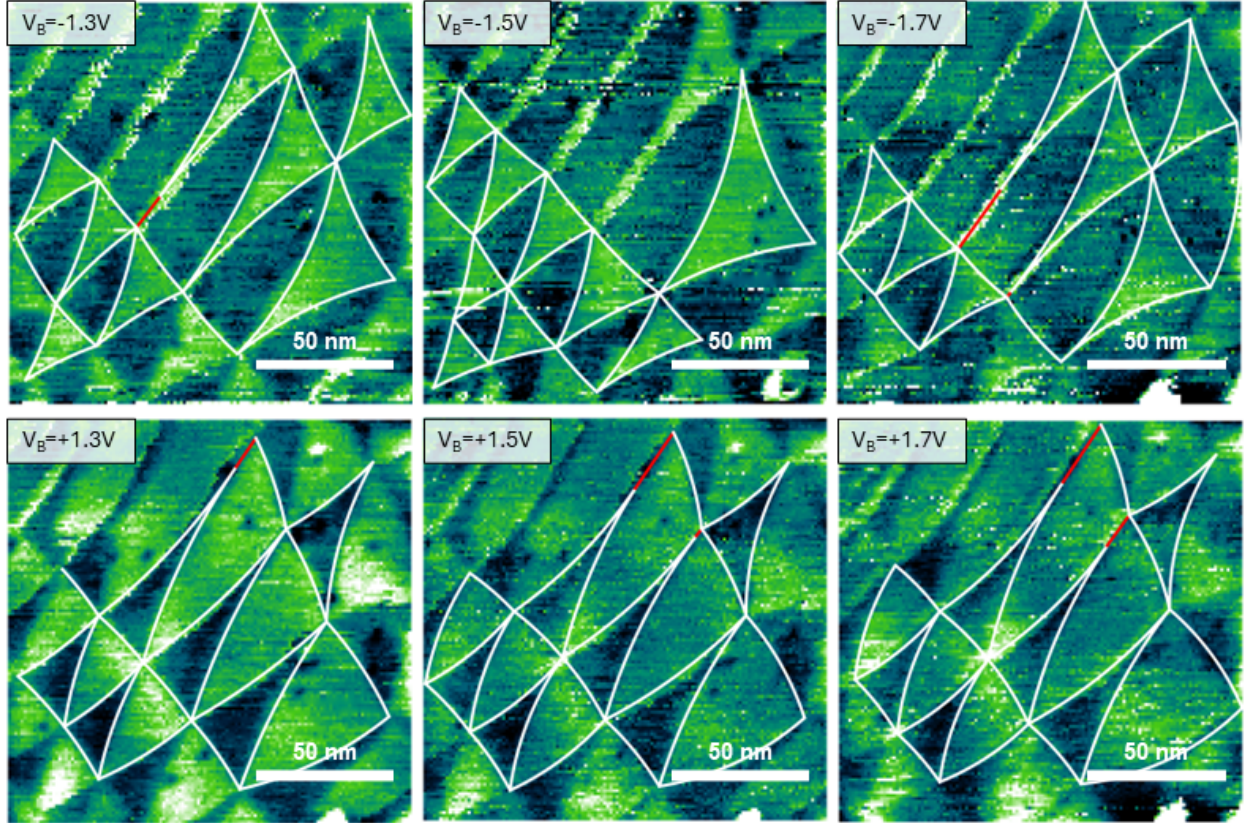


Figure 4.16: Elongated triangle DW fits. Calculated double DW shown in red. Data acquired on Sample 2 with Tip 2 at $I_T = 100 \text{ pA}$ and indicated biases.

4.3.9 Extension of network model for elongated domains

To describe merging of two DWs for elongated domains we modify the model used for equilateral domains [100]. We define an elongated domain as the one having a short DW with internode distance ℓ_3 , and two much longer DWs characterised by internode distance $\ell_{1,2} \gg \ell_3$. To characterise bending energy of each DW we use an expression established earlier [100], $w + \tilde{w} \sin^2(\Phi_{1,2,3})$, where $w = 1.05 \text{ eV}/nm$ is DW energy per unit length in armchair direction, $\tilde{w} = 0.69 \text{ eV}/nm$ is an orientation-dependent part of the energy, and $\Phi_{1,2,3}$ are angles defining local orientation of the DW with respect to the armchair direction. In the model we also take into account opportunity for the two long DWs to merge into a PSD oriented along zigzag direction with energy per unit length $u = 2.45 \text{ eV}/nm$. To describe bending of long DWs we introduce functions, $y_{1,2}(x_{1,2})$ determined in the interval $\mathcal{L} \cos(\alpha_{1,2}) \leq x_{1,2} \leq \ell_{1,2}$, while shape of the short DW is determined by $y_3(x_3)$ in the interval $0 \leq x_3 \leq \ell_3$. Then, local orientation of the DWs is $\Phi_i = \phi_i + \arctan(y'_i)$, $i = 1, 2, 3$, and ϕ_i are angles between direction of the DW in zero electric field and the closest armchair crystallographic axis (see Figure 4.17). To find $y_{1,2,3}(x_{1,2,3})$, $\mathcal{L}$, and $\alpha_{1,2}$ we minimise the following functional

$$\begin{aligned} \varepsilon[y_1(x_1), y_2(x_2)] = & \sum_{i=1,2,3} \int_{\delta_i}^{\ell_i} \left[\left(w + \tilde{w} \frac{(\sin(\phi_i) + y'_i \cos(\phi_i))^2}{1 + y_i'^2} \right) \sqrt{1 + y_i'^2} - 2D\Delta y_i \right] dx_i \\ & + \left[\mathcal{L}u - \frac{\mathcal{L}^2 D\Delta}{4} \sum_{i=1,2} \sin(2\alpha_i) \right] \end{aligned} \quad (4.4)$$

Here, the first term in the integrand describes the orientation-dependent energy of partial dislocations due to their bending ($\sin(\Phi_i) = \frac{\sin(\phi_i) + y'_i \cos(\phi_i)}{\sqrt{1 + y_i'^2}}$), the second term stands for the energy gain ($-2D\Delta$) from increasing area of a domain with the stacking promoted by

the out-of-plane electric field, D/ϵ_0 , which couples to the ferroelectric polarisation density, $\epsilon_0\Delta$, determined by interlayer voltage drop $\Delta = 62mV$ for 3R WS_2 bilayers (ϵ_0 is vacuum permittivity); integration limits are $\delta_{1,2} = \mathcal{L} \cos(\alpha_{1,2})$, $\delta_3 = 0$. Terms outside of the integral allow for merging of the long DWs with formation of the PSD of $\mathcal{L}$ -length projected into the intervals $0 < x_{1,2} < \mathcal{L} \cos(\alpha_{1,2})$. For long DWs this leads to boundary conditions (BCs): $y_{1,2}(\mathcal{L} \cos(\alpha_{1,2})) = \mathcal{L} \sin(\alpha_{1,2})$, $y_{1,2}(\ell_{1,2}) = 0$, in which $\mathcal{L}$ and $\alpha_{1,2}$ are additional variation parameters to be found from minimisation of 4.4. However, for short DW BCs are: $y_3(\ell_3) = y_3(0) = 0$.

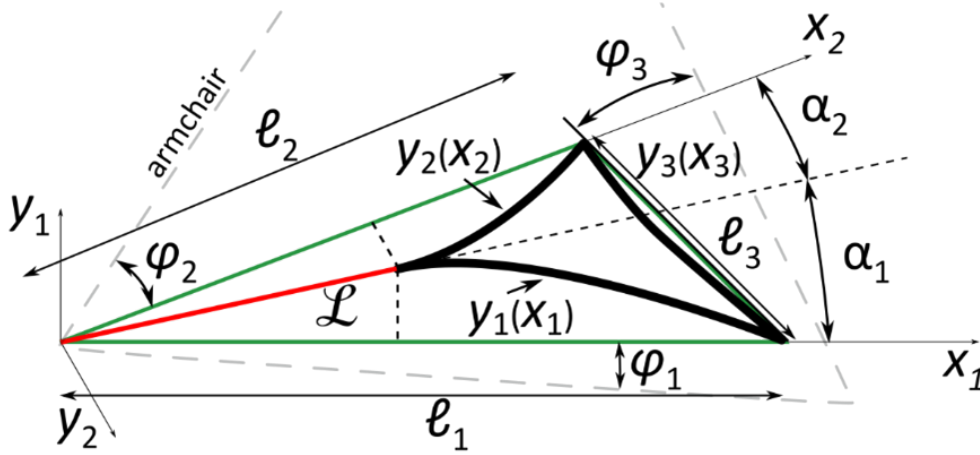


Figure 4.17: Green triangle shows DWs (partial dislocations) surrounding a single elongated 3R domain at zero electric field. Bold black lines show the shape of partial dislocations under out-of-plane electric field. Red straight segment is a streak of PSD formed by merging of the two long DWs. Dashed gray lines show armchair directions for which DW energy is minimal

General solutions of the corresponding Euler-Lagrange equations are expressed via roots of the algebraic equations:

$$\frac{y_i'^3}{(1 + y_i'^2)^{3/2}} - \frac{\frac{w}{\tilde{w}} + 2 - 3 \sin^2 \phi_i}{\cos^2 \phi_i} \frac{y_i'}{\sqrt{1 + y_i'^2}} - \frac{\tan \phi_i}{(1 + y_i'^2)^{3/2}} - \frac{2D\Delta}{\tilde{w} \cos^2 \phi_i} x + C_1 = 0 \quad (4.5)$$

where C_1 is an integration constant. In the limit $\phi_{1,2,3} = 0$, which corresponds to equilateral

domains, solution of 4.5 is reduced to that derived in Reference [100], noting that $\frac{f_i}{\sqrt{1-f_i^2}} = y'_i$ and choosing $C_1 = D\Delta\ell$, which ensures symmetric shape of the bended DWs. Here we solve 4.5 in the limit $y_i'^2 \ll 1$ which is relevant for experimentally observed elongated domains. In this case in 4.5 we leave only terms $\propto y'_i$, which results in parabolic shapes for DWs:

$$y_{1,2}(x_{1,2}) = \frac{D\Delta/\tilde{w}}{\frac{w}{\tilde{w}} + 2 - 3\sin^2\phi_{1,2}} (\ell_{1,2} - x_{1,2}) \left(x_{1,2} - \frac{\mathcal{L}^2 \cos^2(\alpha_{1,2})}{\ell_{1,2}} \right), \quad (4.6)$$

$$y_3(x_3) = \frac{D\Delta/\tilde{w}}{\frac{w}{\tilde{w}} + 2 - 3\sin^2\phi_3} (\ell_3 - x_3) x_3. \quad (4.7)$$

In Equation 4.6, parameters of PSD are determined by touching condition of the DWs at $x_{1,2} = \mathcal{L} \cos(\alpha_{1,2})$, which leads to minimum of functional 4.4:

$$\begin{cases} \tan(\alpha_1) = \frac{D\Delta/\tilde{w}}{\frac{w}{\tilde{w}} + 2 - 3\sin^2\phi_1} \frac{(\mathcal{L} \cos(\alpha_1) - \ell_1)^2}{\ell_1}, \\ \tan(\alpha_2) = \frac{D\Delta/\tilde{w}}{\frac{w}{\tilde{w}} + 2 - 3\sin^2\phi_2} \frac{(\mathcal{L} \cos(\alpha_2) - \ell_2)^2}{\ell_2}, \\ \alpha_1 + \alpha_2 = \arccos\left(\frac{\ell_1^2 + \ell_2^2 - \ell_3^2}{2\ell_1\ell_2}\right). \end{cases} \quad (4.8)$$

To solve Equation 4.7 we exclude $\mathcal{L}$ with the help of the first two equations and, then, using the third equation determine $\alpha_{1,2}$. With known $\alpha_{1,2}$ length of the PSD streak reads as:

$$\mathcal{L} = \frac{\ell_1 - \sqrt{\ell_1 \frac{(\frac{w}{\tilde{w}} + 2 - 3\sin^2\phi_1)}{D\Delta/\tilde{w}} \tan(\alpha_1)}}{\cos(\alpha_1)} = \frac{\ell_2 - \sqrt{\ell_2 \frac{(\frac{w}{\tilde{w}} + 2 - 3\sin^2\phi_2)}{D\Delta/\tilde{w}} \tan(\alpha_2)}}{\cos(\alpha_2)}. \quad (4.9)$$

4.3.10 How we obtain the experimental perfect screw dislocation length

$$L_{\text{exp}}$$

In Figure 4.15(c), experimental PSD length L_{exp} is plotted against predicted PSD length $\mathcal{L}$. The theoretically predicted separation between the partial screw dislocations that run close to each other just before they reach the merging point is comparable to our image pixel resolution which was $\sim 1.6\text{nm}$. Therefore, in our STM images, what we observe as merged length is an overestimation of the PSD length by an amount L_{res} (Figure 4.18), which can be calculated in each case from Equation 4.9 taking into account the pixel size. To account for this, when calculating L_{exp} reported in Figure 4.15(c), for each domain, the measured length of the merged DW in the STM image, L_{stm} (Supplementary 4.18) was reduced by L_{res} , $L_{\text{exp}} = L_{\text{stm}} - L_{\text{res}}$.

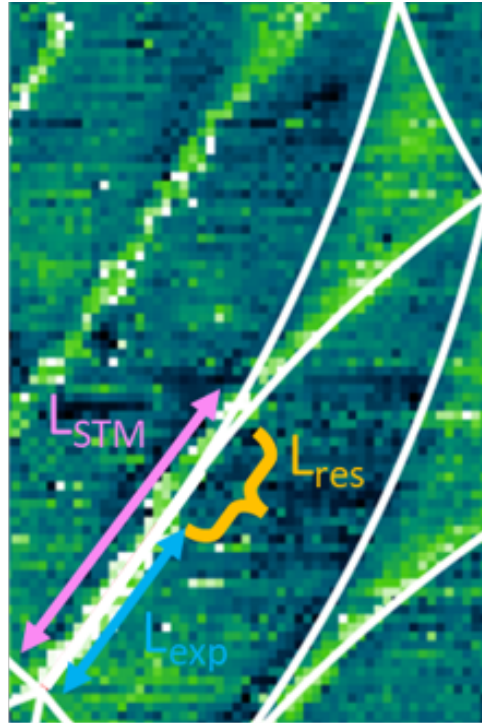


Figure 4.18: How we obtain the experimental PDS length L_{exp} .

We note that in some elongated triangles, at some biases, no merging is predicted to occur: a domain node is reached before the partial screw dislocations can merge.

4.3.11 Hysteresis

In order to investigate memory effects in DW bending, the response of the DWs to cycling the tip-sample bias was investigated. A region was repeatedly scanned, with the bias being adjusted each scan, cycling from $-1.3V$ to -1.7 , and back to $-1.3V$, as shown in Figure 4.19(a). The DWs were fit with the equilateral triangle model presented in 4.3.2. However, rather than finding the value of displacement field D which produces the best fit, the best fitting value of $B' = \frac{2D'P}{0\tilde{w}}$ was found. Here, B' is the "Bending parameter" and has units of inverse length. Larger B' indicates more bending. D' is the apparent displacement field, which will differ from the actual displacement field if there are memory effects.

In the absence of memory effects, B' will vary monotonically with tip bias. If there are consistent differences in B' as a function of V_B when the bias is being swept up vs. down, that may indicate hysteresis. However, as shown in Figure 4.19(b), no such differences could be observed beyond the measurement uncertainty.

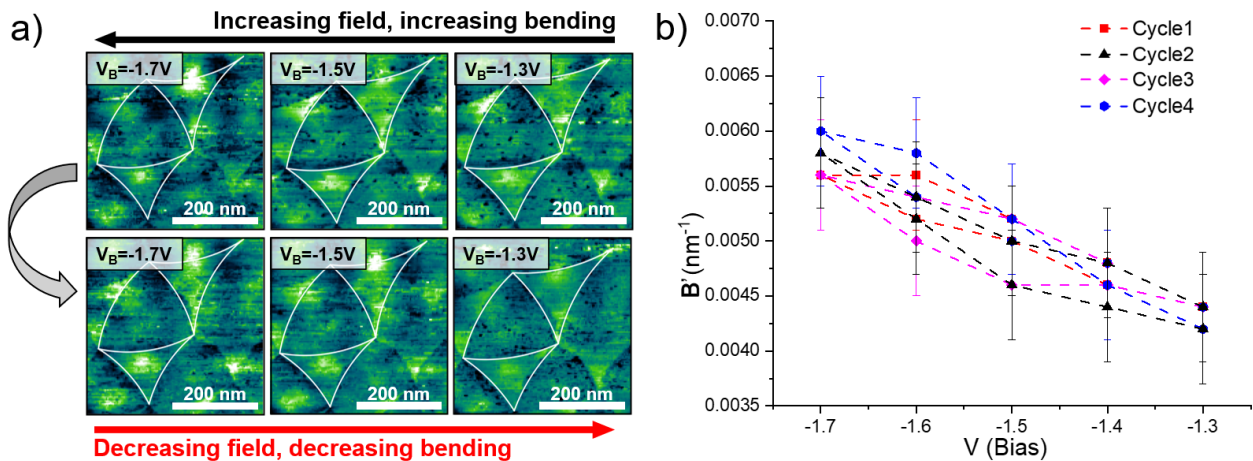


Figure 4.19: Hysteresis experiment. (a) Example cycling of tip bias with equilateral triangle model DW fits. (b) Bending parameter B' vs. V_B for four cycles.

Other works have observed evidence of hysteresis in DW bending with transport measurements [134, 146, 153] and TEM [145], the latter of which suggests that pinning of the domain walls at defects may be responsible. In [145], pinning effects were observed to stall DW movement by seconds or less, which may explain why our measurement fails to capture hysteresis effects; STM images take tens of seconds to capture. This may also account for why defects were not observed to play a roll in DW dynamics in this work.

4.3.12 Conclusion

To summarize, we have demonstrated that for each marginally twisted sample the analysis of the ferroelectric domain network can give detailed information about the deformations in the assembled layers. These deformations lead to the variation of domain sizes across the network, producing a variety of switching conditions for individual domains. We demonstrate that one can achieve full local control over the domain network, by squeezing out the unfavorable polarization from the larger and elongated domains. This happens through merging pairs of partial dislocations into a perfect dislocation. Note that, despite an apparent disappearance of the unfavorably polarized domains, the surface polarization remains reversible, as, upon the reversed bias, perfect "full" dislocations split up into pairs of partial dislocation, nucleating domains of opposite stacking order.

We also note that usually switching of ferroelectric polarization across a large volume/area of ferroelectric material is associated with hysteresis. In the context of interfacial ferroelectricity, such hysteresis has been observed (both in SEM imaging and transistor operation) in marginally twisted MoS₂ bilayers with extremely large domain sizes [98]. In that case, DW pinning occurred due to defects encountered by the DW propagation to long distances. In $0.2^\circ - 1.5^\circ$ twisted structures with relatively small domains, local deformation of DWs, which ends are pinned to the XX sites of the DWN, explore local clean areas of high-quality material without pinning centers. As a result, no hysteresis appears, and we

achieve reversible local control of ferroelectric dipole moments in the studied TMD bilayer.

4.3.13 Methodological details

We computed the charge density in Figure 4.3(a) using density functional theory implemented in Quantum ESPRESSO [168, 169], constructing a supercell with a pair of mirror-reflected XM' and MX' bilayers separated by a large vacuum interval, as in Ref. [150] We exploited full-relativistic projector augmented wave pseudo-potentials with Perdew-Burke-Ernzerhof exchange correlation functional, kinetic energy and charge density cutoffs – $90Ry$ and $1000Ry$, respectively, and $23 \times 23 \times 1$ reciprocal space grid. Parameters of WS₂ bilayer crystal structure were taken from Ref. [170]. This work was performed by Vladimir Enaldiev and Vladimir I. Fal'ko.

The sample was assembled using the tear-and-stack technique [140, 171]. WS₂ crystals were purchased from HQ Graphene and were mechanically exfoliated onto Si/SiO₂ substrates. Monolayer WS₂ was identified optically, and the thickness was confirmed with atomic force microscopy (AFM). Suitable graphite flakes were identified and were picked up with a polydimethylsiloxane (PDMS) stamp covered with Polypropylene carbonate (PPC) film on a glass slide. The graphite on the polymer stamp was then used to pick up monolayer WS₂. The two layers of WS₂ correspond to two halves of a large flake, allowing for precise rotational control. The PPC film was then cut and the 2D material stack was transferred onto a Si/SiO₂ substrate coated with Ti/Au ($5nm/150nm$). The sample was then annealed under ultra-high vacuum at $300^{\circ}C$ for several hours. The surface was cleaned using an AFM tip [172, 173]. STM measurements were performed at pressures below $10^{-9}Torr$, at RT. For STS we used bias modulation of $5.0mV$, $1.325kHz$.

Chapter 5

Out-of-plane relaxation and flat electronic bands in anti-parallel aligned transition metal dichalcogenides homobilayers

While Chapter 4 examined the dynamics of in-plane relaxation and the emergence of interfacial ferroelectricity, this chapter focuses on the band structure of bilayer transition metal dichalcogenides (TMDs), and the role of out-of-plane relaxation. This chapter presents a modified version of the publication **L. Molino, L. Aggarwal, I. Maity, R. Plumadore, J. Lischner, A. Luican-Mayer. "Influence of atomic relaxations on the moiré flat band wavefunctions in antiparallel (AP) twisted bilayer WS₂". *Nano Lett.* 23, 24, 11778–11784 (2023).**

5.1 Band structure in twisted bilayer transition metal dichalcogenides

Several factors contribute to the electronic structure of twisted bilayer TMDs. In a twisted bilayer, the moiré unit cell is much larger than monolayer atomic lattice unit cells, and therefore has a smaller, "mini", Brillouin zone (BZ), which is populated by folding in the band of the monolayers. Technically, this is only the case if the twisted bilayer is at one of

the specific angles where the two layers are commensurate, otherwise the system is only quasi-periodic, and cannot be properly described as having a BZ, though this distinction can often be neglected in practice. The band structure of the mini-BZ is modulated through interlayer interaction. In- and out-of-plane relaxation also have a profound effect on the electronic structure [147, 156].

The resulting band structure can be understood by examining the local density of states (LDOS) at the high symmetry sites. First principles work has predicted that the factors listed above will cause the valence band (VB) and conduction band (CB) edges (VBE, CBE) to occur at different energies at different moiré sites, with the VBE being particularly sensitive since it is composed of p-character orbitals, with large out-of-plane extents [147, 156]. With this in mind, the moiré pattern can be thought of as a periodic potential, whose "depth" is equal to the difference between the minimum and maximum energies of the band edges [142, 147]. Carriers can be confined by this "potential", leading to enhanced correlation, which manifests as flat bands and can be observed as van Hove singularities (sharp peaks in the density of states (DOS) arising from flat bands).

Scanning probe techniques are invaluable in probing the electronic structure of moiré materials, in particular, due to their ability to measure the LDOS at the atomic length scale. Scanning tunneling spectroscopy (STS) allows for direct measurement of the LDOS, which allows for measurement of the moiré potential and flat band bandwidths, and allows for the visualization of the confined wave functions in real space. STS is sensitive to both Γ - and K-point states and can distinguish between the two by measuring their height dependence, often done by switching between constant current and constant height measurement modes. Though details vary with materials, layer alignment, and twist angle, several features appear to be common to these systems. In moiré patterns and reconstructed domains, the periodic potential is observed with a depth on the order of hundreds

of meV [83, 87, 91]. The moiré potential is a non-monotonic function of the twist angle and is observed to be at a maximum for moiré periods around $15nm$ in some systems [83]. This moiré potential gives rise to one or more flat bands, with bandwidths on the order of tens of meV [81, 87]. These flat bands are derived from Γ - and K-point wavefunction on the VBE, and K-point wavefunction of the CBE. The Γ -point flat bands arise largely due to interlayer coupling, due to their p-character and out-of-plane extent, while the K-point flat bands are more often attributed to monolayer deformation [79, 81, 86, 88, 91]. In cases that feature in-plane reconstruction, the shape of the moiré potential well is sensitive to changing domain geometry, with the moiré potential going from a network of roughly circular wells to more triangular wells in the case of a parallel- (P-) aligned bilayer [87, 142]. This change in geometry modulates the flat bands, influencing the number and energies of the confined states, and the geometry of the confined wavefunctions.

Moiré buckling

While in-plane relaxation has been observed at marginal twist angles (see Section 4.1), out-of-plane relaxation (which results in corrugation or "buckling" of the bilayer periodic with the moiré pattern) occurs in all moiré patterns in bilayer TMDs. This corrugation can be observed experimentally [81] and has a significant impact on the electronic structure of the bilayer as shown with first principles methods [81, 147].

In Section 5.2, a modified version of the publication **L. Molino, L. Aggarwal, I. Maity, R. Plumadore, J. Lischner, A. Luican-Mayer. "Influence of atomic relaxations on the moiré flat band wavefunctions in antiparallel (AP) twisted bilayer WS_2 ". *Nano Lett.* **23**, **24**, 11778–11784 (2023)** is presented. In this work, the electronic structure of 57° twisted WS_2 is examined with scanning tunneling microscopy (STM). This structure falls within the AP unreconstructed moiré regime. Through comparison to first principles calculations, this work examines the role of out-of-plane relaxation on the electronic structure

and in particular the spatial localisation of the flat band wavefunction. This work finds evidence that moiré buckling is suppressed in real samples due to substrate effects, which influence the spatial localisation of the wavefunctions on the VBE.

The experiments in this work was planned by Adina Luican-Mayer and Laurent Molino (L.M.). The samples were prepared by L.M. The data was collected and analysed by L.M. and Leena Aggarwal (L.A.), with advice from Ryan Plumadore, using software written by L.M.. Indrajit Maity and Johannes Lischner provided the first principles calculations and contributed to the interpretation of the data. The text was drafted by L.M. and L.A. and edited by all authors.

5.2 Influence of atomic relaxations on the moiré flat band wavefunctions in antiparallel twisted bilayer WS₂

A note on notation

In this chapter, the MM', XX', and 2H-AP stackings are referred to as B^{MM}, B^{XX}, and AA' respectively. This is to emphasise these structural differences between different stacking orders.

5.2.1 Introduction

When a pair of two-dimensional (2D) materials are stacked vertically and then rotated relative to each other, a moiré superlattice is created. Electrons in such a superlattice experience a moiré potential which favors electron localization in specific stacking regions, reduces the electrons' kinetic energy, and results in the formation of flat bands with enhanced electron-electron interactions, promoting phenomena such as superconductivity, Mott insulating phases, topological phases, coupled spin-valley states, and interlayer excitons [174–180].

In contrast to graphene bilayers which exhibit flat bands at a specific "magic" twist angle, bilayers of TMDs offer a much larger range of twist angles at which flat bands are realized [80, 81, 87, 142, 181–183], opening broader possibilities for creating previously inaccessible correlated systems. Both TMD homobilayers (in which two layers of the same material are combined) and heterobilayers (in which two different TMD monolayers are combined) have been studied. In heterobilayers, the length scale of the moiré pattern is less sensitive to the twist-angle than in homobilayers, leading to reduced twist angle disorder in large samples. As a result, to date, several heterobilayer TMDs such as WSe_2/WS_2 [34, 81], MoS_2/WS_2 [164, 184–186], $\text{MoS}_2/\text{WSe}_2$ [79, 80] and $\text{WSe}_2/\text{MoSe}_2$ [83] have been investigated experimentally, with reports of correlated phenomena such as superconductivity, Mott insulating phases, generalized Wigner crystals, and more [81, 105, 181, 187]. Moiré patterns of TMD homobilayers are highly sensitive to the twist angle, and thus expected to exhibit more twist-angle disorder. As a consequence, these systems are less studied despite having great potential for inducing strong moiré potentials [95, 142, 147, 176, 188]. For example, recent scanning probe microscopy experiments on a $\text{WSe}_2/\text{WSe}_2$ homobilayer have demonstrated twist-angle-dependent lattice reconstructions near a 60° twist angle resulting in multiple energy-separated ultra-flat VBs for long moiré wavelengths ($6\text{nm} - 12\text{nm}$) [87].

Semiconducting TMDs have metal and chalcogen atoms occupying the lattice sites in their unit cell breaking sub-lattice symmetry. For this reason, twisted TMD bilayers fall into two classes: P-aligned bilayers with a twist angle close to 0° , and antiparallel- (AP-) aligned bilayers with twist angles near 60° . These two classes exhibit different stacking configurations in the moiré unit cell which results in different atomic relaxations in the form of both out-of-plane buckling and in-plane reconstructions. In-plane reconstructions can be understood as the result of the layers deforming to increase the area of the energetically preferred

stacking order [130, 142, 147, 148]. For very small twist angles (or twist angles very close to 60°), this reconstruction produces networks of uniform stacking order domains separated by highly strained domain walls. In the case of P-aligned TMD homobilayers, the system tends towards a network of triangular stacking order domains. Due to the lack of inversion symmetry, these domains host interlayer charge transfer leading to an out-of-plane ferroelectric dipole moment [83, 89, 130, 147]. In the case of AP-aligned TMD homobilayers, no such charge transfer occurs. While AP systems do form domain wall networks at angles very close to 60° , they generally exhibit less pronounced in-plane reconstructions than P-aligned bilayers at a given twist-angle offset, leading to a more smoothly varying periodic lattice distortion over the moiré unit cell [95]. In all cases, both out-of-plane buckling and in-plane reconstruction have a profound impact on the electronic properties of TMD homobilayers. In-plane and out-of-plane deformations cause the simple band-folding description of a moiré pattern band structure to break down, for example, causing a modification in the real-space position of the VBE wavefunctions. Strain is furthermore critical to wavefunction localisation responsible for strong correlated effects observed in these systems [142, 147].

As the field of moiré-induced flat band physics progresses, it is important to explore a larger range of homobilayer systems, especially using scanning probe techniques that can directly reveal the local twist angle. Here, we report room temperature (RT) STM/STS studies of moiré superlattices of $\approx 6nm$ wavelength in the WS_2/WS_2 bilayer system near 60° twist angle or antiparallel (AP) alignment, together with extensive large-scale density functional theory (DFT) calculations. Importantly, we demonstrate that the localization of the flat-band wavefunctions depends sensitively on the degree of lattice relaxations.

5.2.2 Results

We fabricated the AP WS_2 twisted bilayer using a variation of the "tear-and-stack" dry transfer method (Section 5.2.4) and performed RT STM/STS experiments, as indicated

schematically in Figure 5.1(a). Across the entire sample, we identified moiré patterns with a range of periods ($6nm - 15nm$) (Figure 5.2), corresponding to a twist-angle range of $57.0^\circ - 58.8^\circ$, indicating the presence of twist-angle disorder within the AP-WS₂ sample. A large area of uniform hexagonal moiré pattern with a period of $6.0nm \pm 0.2nm$ (corresponding to a twist angle of $57.00^\circ \pm 0.08^\circ$) is shown in Figure 5.1(b). A zoomed-in scanning tunnelling micrograph of this pattern in Figure 5.1(c) highlights the unit cell and the different high-symmetry stacking regions within it ($B^{S/S}$, AA' , $B^{W/W}$), with corresponding atomic configurations described in Figure 5.1(d).

A simulated STM topograph of a 56.86° AP-twisted WS₂ bilayer obtained from DFT calculations based on the Tersoff-Hamann approximation [122] is shown in Figure 5.1(e). Before the DFT calculations, the relaxed atomic positions of the twisted bilayer, shown in Figure 5.1(f), were obtained using classical force fields (see Methods). The difference between the tunnelling matrix elements of the high symmetry sites in this sample are primarily due to the out-of-plane buckling of the top layer, rather than the differences in the orbitals at different sites, due to the exponential dependence of the tunnelling matrix element on the tip-sample distance. The simulated topograph is in good agreement with the experimental micrograph of Figure 5.1(c). In particular, the bright regions correspond to $B^{S/S}$ stacking. This stacking exhibits the largest buckling and therefore also the largest tunnelling matrix element.

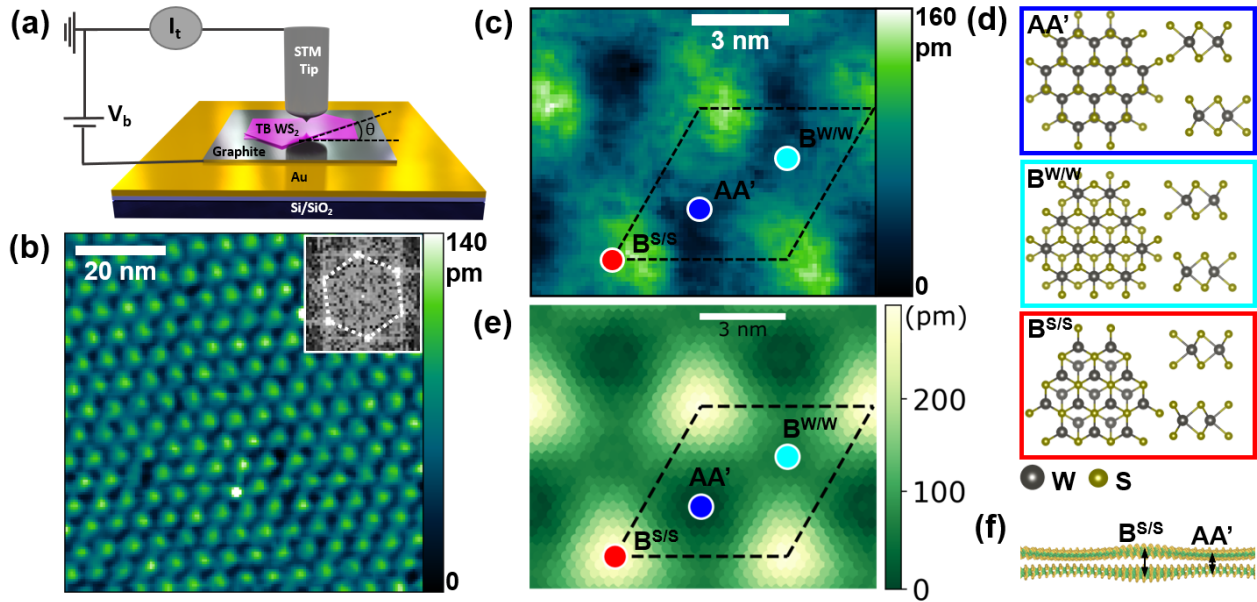


Figure 5.1: (a) Schematic of the STM experiment: a twisted bilayer WS_2 with $\theta \approx 60^\circ$ is prepared on a graphite/Au substrate. (b) STM topography showing a region with $6.0 \text{ nm} \pm 0.2 \text{ nm}$ moiré pattern, corresponding to a twist angle of $57.00^\circ \pm 0.08^\circ$ (scanning parameters: bias voltage $V_b = -1.3 \text{ V}$, tunneling current $I_t = 100 \text{ pA}$). Inset: Fourier transform of the moiré pattern showing hexagonal symmetry. (c) STM topograph of $6.0 \text{ nm} \pm 0.2 \text{ nm}$ moiré pattern (scanning parameters: $V_b = -1.3 \text{ V}$, $I_t = 150 \text{ pA}$). The dashed rhombus corresponds to the moiré unit cell, with high-symmetry stacking regions ($\text{B}^{\text{S/S}}$, AA' , $\text{B}^{\text{W/W}}$) indicated by circles. (d) Atomic structure of the three high-symmetry stackings present in an antiparallel aligned twisted WS_2 homobilayer. (e) Simulated STM topography for a 56.86° twisted AP WS_2 homobilayer obtained from first-principles DFT calculations on a relaxed atomic structure. (f) Side view of twisted bilayer WS_2 showing out-of-plane buckling, exaggerated by a factor of ten for clarity. Locations of maximum and minimum interlayer spacing are indicated. The maximum interlayer spacing, corresponding to $\text{B}^{\text{S/S}}$ stacking, is 8% larger than the minimum interlayer spacing, corresponding to AA' stacking.

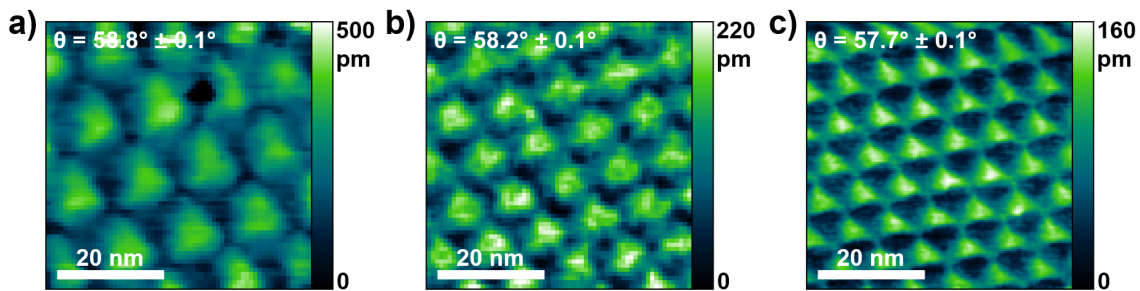


Figure 5.2: (a-c) STM topography with three different twist angles as indicated, corresponding to moiré wavelengths of $14 \text{ nm} \pm 1 \text{ nm}$, $10.1 \text{ nm} \pm 0.7 \text{ nm}$, $7.9 \text{ nm} \pm 0.4 \text{ nm}$ respectively. Data were taken at $V_b = -1.3 \text{ V}$, $I_t = 100 \text{ pA}$.

To explore the local electronic properties of the moiré superlattice in Figure 5.1(b), we performed STS measurements. In Figure 5.3(a) we present the average tunnelling conductance (dI/dV) acquired over five moiré periods. A spatially resolved presentation of this measurement, showing modulation of the LDOS by the moiré pattern, is given in Figures 5.4. The band gap is calculated to be $1.03\text{eV} \pm 0.02\text{eV}$, as shown in Figure 5.5. Two notable features are present in the spectrum: a first one (denoted V_1) near the VBE, with an energy of $\approx -1.0\text{eV}$, and a second feature V_2 deeper in the VB at $\approx -1.7\text{eV}$.

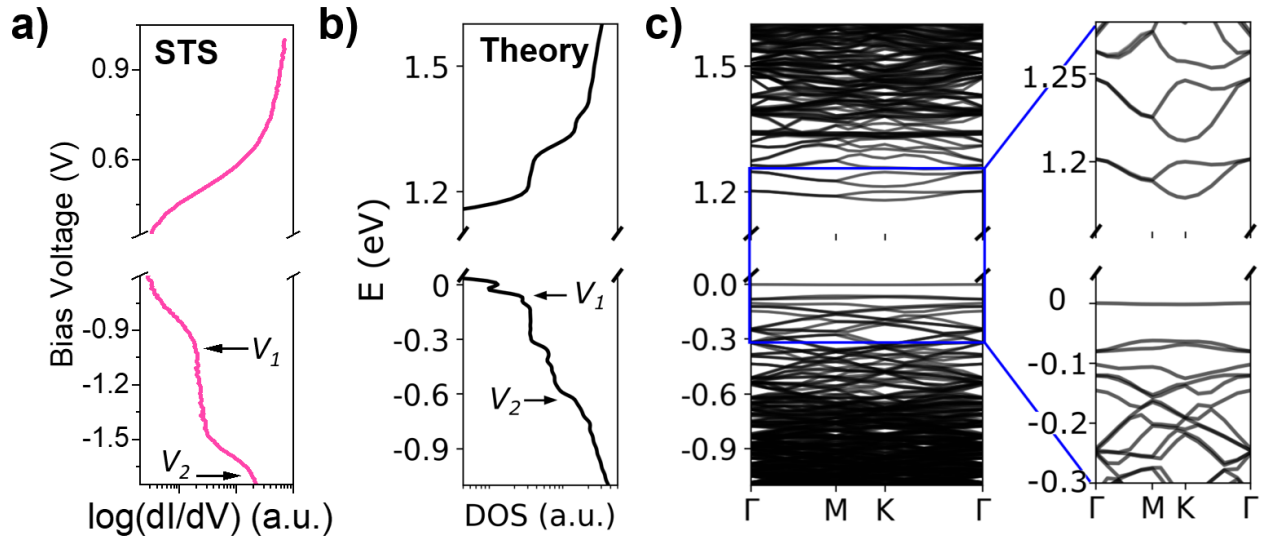


Figure 5.3: (a) Average of scanning tunneling spectra acquired over the moiré region indicated in Supplementary Figure 5.5. (b) Calculated DOS for 56.86° twisted bilayer WS_2 including atomic relaxations. The VB maximum is set to 0. (c) Electronic band structure of 56.86° twisted bilayer WS_2 including atomic relaxations. The blue rectangle represents a zoom into the band structure around the band gap, for clarity.

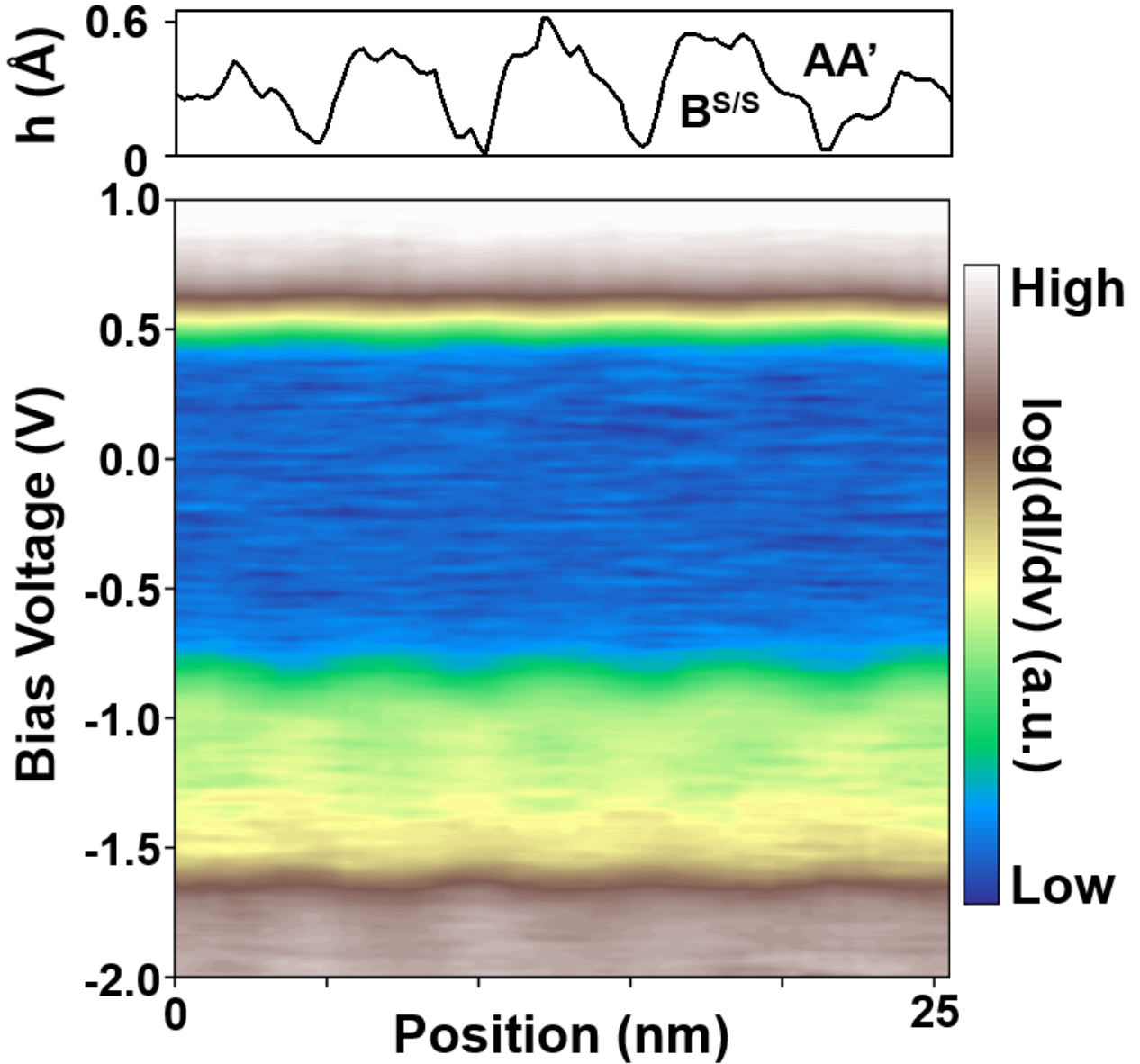


Figure 5.4: STS line profile crossing 4.5 moiré periods, demonstrating moiré modulation around $V_1 = -0.9V$ and $V_2 = -1.6V$. The above figure indicates the height profile along the line indicated in the STM topography in Figure 5.5(a).

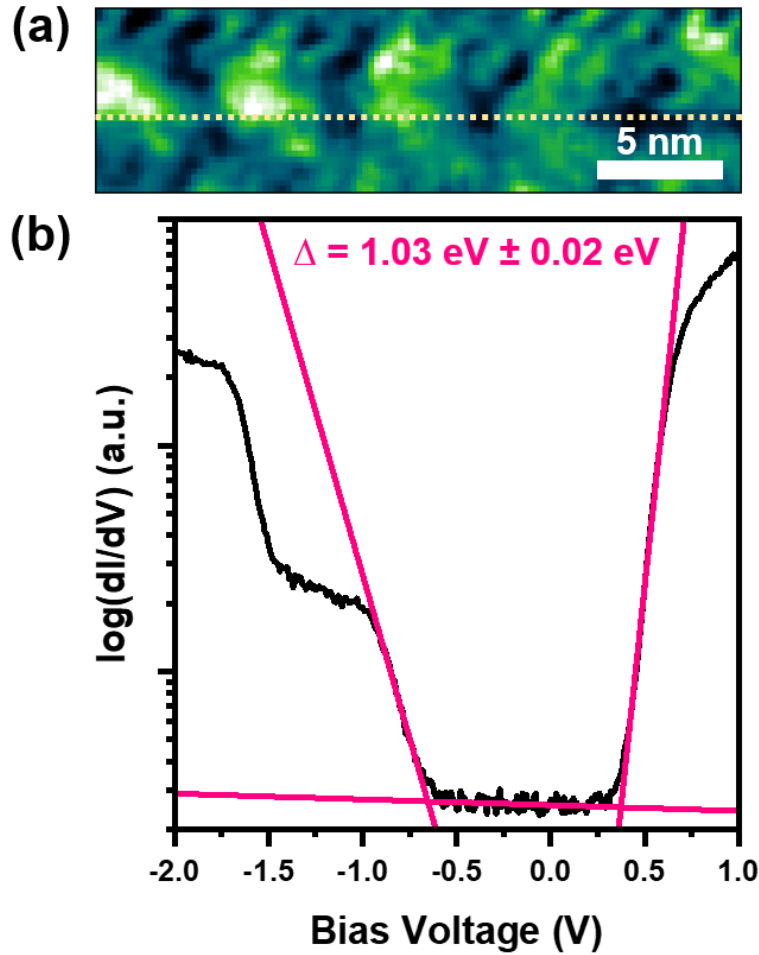


Figure 5.5: **(a)** Area in which the spectra presented in Figure 5.3(a) were collected. Curve in Figure 5.3(a) is the average of the curves collected along the indicated line. **(b)** band gap estimation of scanning tunneling spectroscopy curve corresponding to Figure 5.3(a). In a log plot, linear region of the VBE and CBE, and the band gap, are identified, and used to fit lines. The intersections of these lines correspond to the VBE and CBE.

These two features are also found in the DOS calculated using DFT for the relaxed atomic structure, as shown in Figure 5.3(b). The energy separation between the two features is found to be 0.7 eV , in excellent agreement with the experimental result. We note that the VBE of the calculated DOS is much sharper than in the experiment, which is likely a consequence of thermal broadening (Figure 5.6).

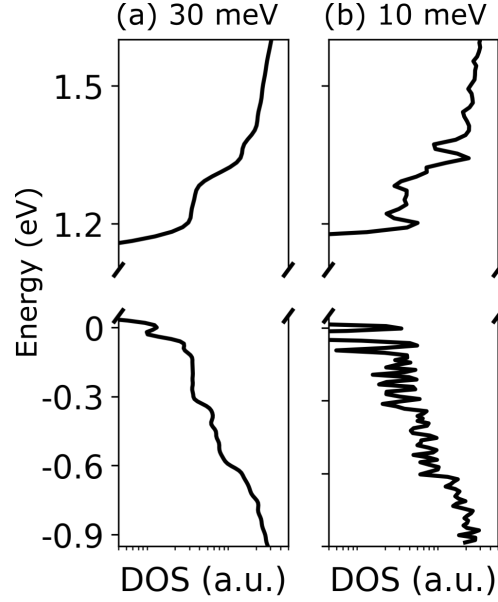


Figure 5.6: (a) DOS with Gaussian smearing corresponding to RT thermal energy, compared to (b) DOS with Gaussian smearing corresponding to approximately $100K$.

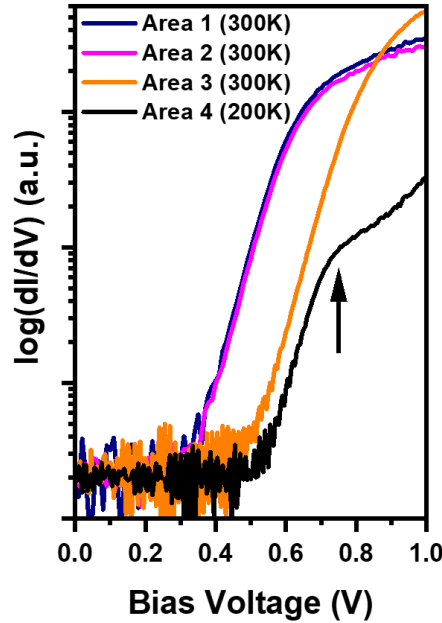


Figure 5.7: STS of CB over all moiré sites. Areas 1, 2, and 3 correspond to those examined in Figure 5.8 panels (a), (b), and (c), respectively. The CB was consistently featureless over the range of energies studied, with the exception of a feature at 750 meV in Area 4, which may be visible due to the lower temperature of this measurement. Scanning parameters: $V_B = 1.3V$, $I_T = 150pA$.

No significant features were observed on the CBE at RT. However, preliminary data collected at $200K$ does suggest that there may be a peak near $750mV$, as shown in Figure 5.7.

To reveal the origin of the observed features close to the VBE, we also present the DFT band structure calculation of the twisted bilayer in Figure 5.3(c) for the same range of energies as the experimental data. This shows that the highest VB is extremely flat with a bandwidth of $2meV$. Approximately $60meV$ below the highest VB we find another pair of relatively flat bands which contribute to the sharp feature V_1 . We also identify another sharp feature in the DOS $0.7eV$ below the V_1 . Note that the V_1 feature arises from the presence of several bands near the VBE, and not the $2meV$ band uniquely.

In Figure 5.8(a-c) we present scanning tunnelling spectra collected at AA' and B^{S/S} stacking regions taken on three areas with slightly different twist angles: $57.0^\circ \pm 0.3^\circ$, $57.1^\circ \pm 0.1^\circ$ and $57.4^\circ \pm 0.2^\circ$ respectively. The insets show the associated topographic image, including the high-symmetry points and unit cell. These assignments are performed by examining a larger region of the moiré lattice and comparing the apparent heights of different sub-lattices. Example high symmetry point assignments are given in Figure 5.9.

The spectra taken at the AA' and B^{S/S} sites show that the VB onset occurs at the B^{S/S} site, suggesting that the highest-lying VB is localised at this site (indicating that the localised state associated with V_1 is *not* the highest lying VB). The difference between the spectra at the two sites is more pronounced for the $57.1^\circ \pm 0.1^\circ$ case, compared to the other two angles, indicating that the electronic structure is highly sensitive to the local twist angle.

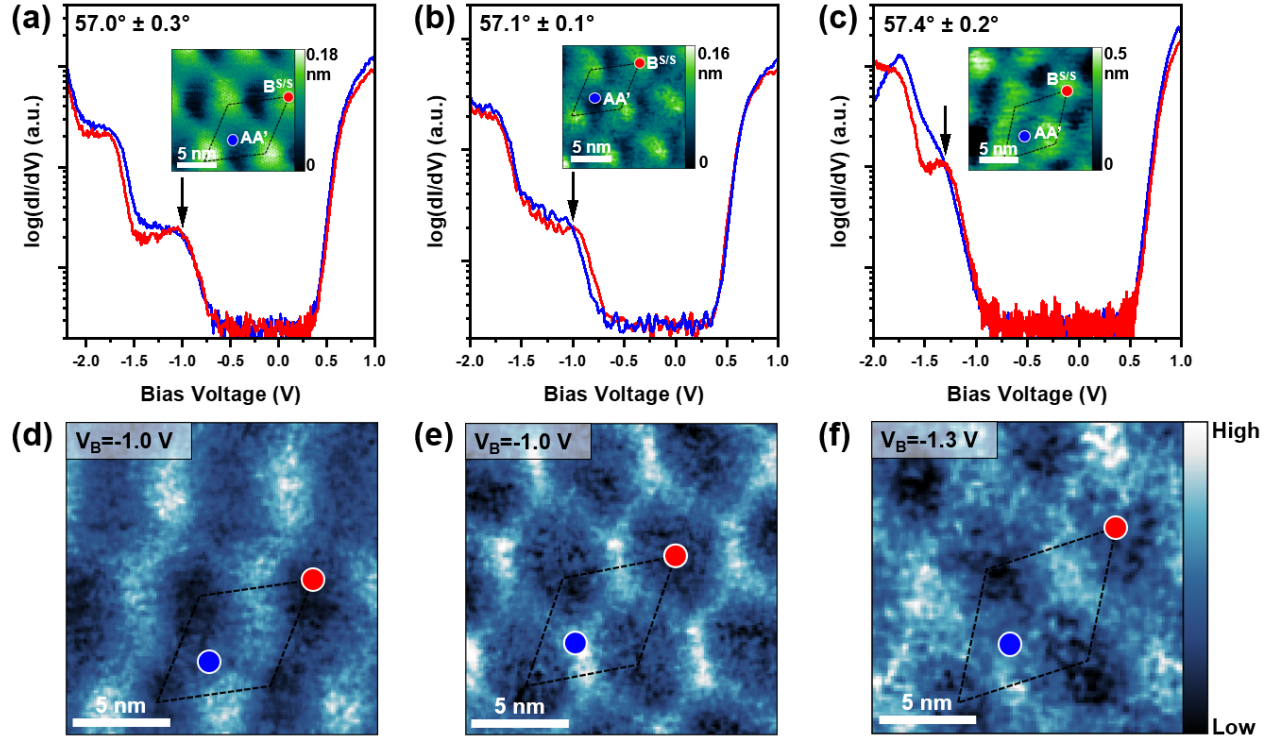


Figure 5.8: (a-c) Scanning tunneling spectra acquired at high symmetry sites in three areas having different twist angles, as indicated. Inset: Topographic maps with red and blue circles indicating the positions associated with the spectra. Topographic maps acquired at $V_b = -1.3$ V, $I_t = 150$ pA for (a) and (c), and $V_b = -1.3$ V, $I_t = 100$ pA for (b). (d-f) dI/dV maps corresponding to (a), (b) and (c) respectively, at indicated bias voltages (tunneling current $I_t = 100$ pA). The high symmetry sites and the moiré unit cell are indicated in each map.

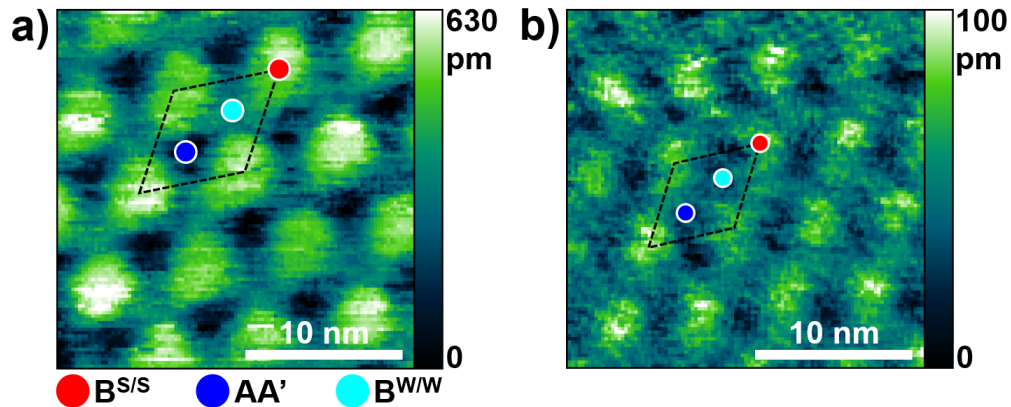


Figure 5.9: STM topography of approximately 6 nm moiré with high symmetry sites identified. Scanning parameters: $V_B = -1.3$ V, $I_T = 100$ pA.

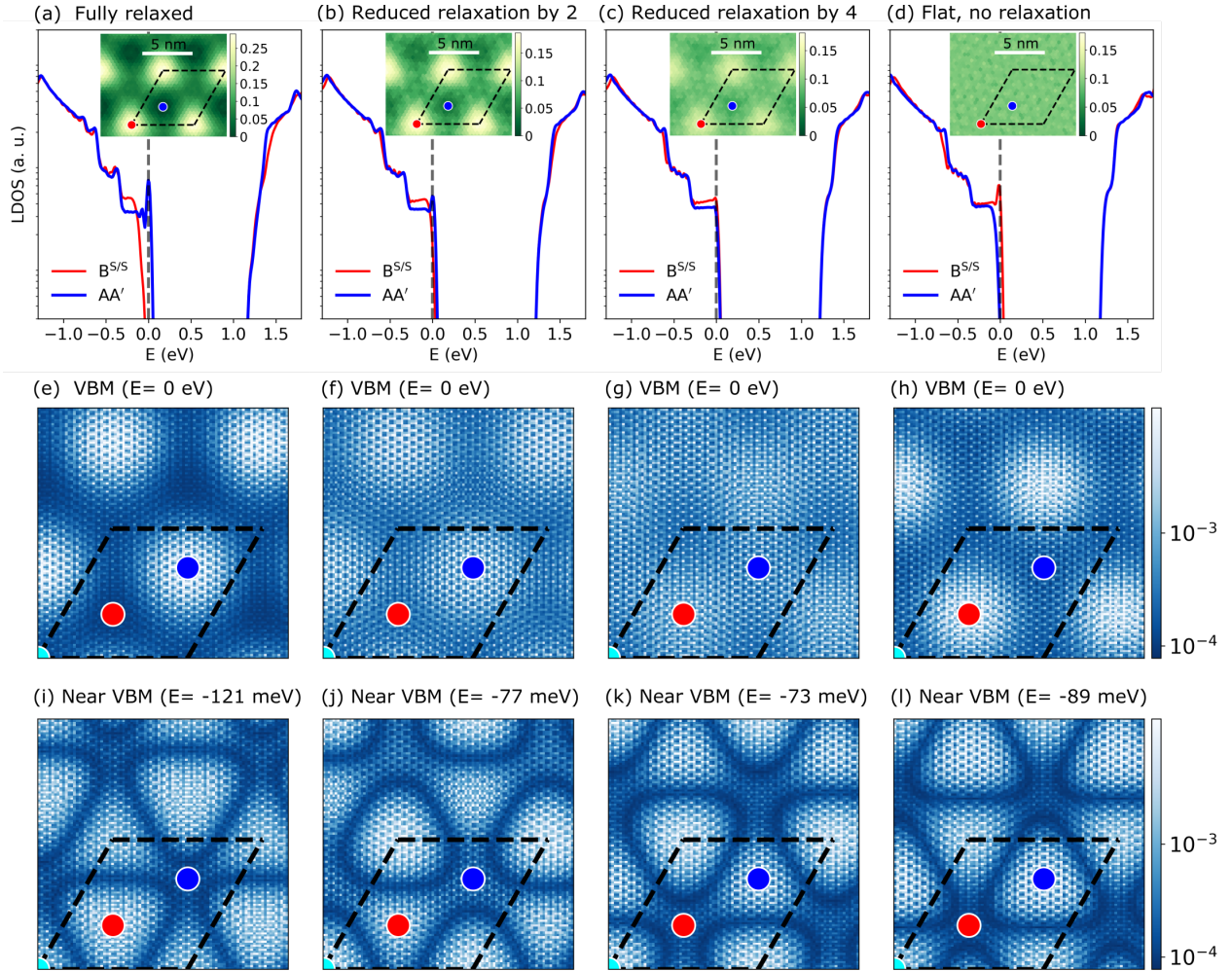


Figure 5.10: Calculated LDOS from DFT for a free-standing twisted bilayer **(a)** including the full atomic relaxations, **(b)** with all atomic displacements reduced by a factor of 2 compared to the fully relaxed result, **(c)** with all atomic displacements reduced by a factor of 4 compared to the fully relaxed result and **(d)** without any atomic relaxations. The VB maximum is set to 0. The insets show the calculated STM topographs. The associated colour bars indicate variation in height in nm. **(e-h)**: Squared wavefunctions of the highest VB at the Γ -point of the moiré BZ for the atomic structures shown in the top panel. **(i-l)**: Squared wavefunctions of a deeper lying VB at the Γ -point of the moiré BZ for the atomic structures shown in the top panel.

Taking advantage of the spatial resolution of a STM/STS experiment, we acquired dI/dV maps in vicinity of the V_1 feature presented in Figure 5.8(d-f). These maps reveal the symmetry of the moiré pattern and demonstrate that the feature V_1 is associated with localised

states that form a hexagonal pattern with high intensity on the AA' sites.

To further understand the experimental findings, we calculated the LDOS at the AA' and B^{S/S} sites using DFT. Figure 5.10(a) shows the result for a fully relaxed free-standing twisted bilayer (i.e. a bilayer in free space without a substrate), while Figure 5.10(b-d) show the calculated LDOS for partially and finally unrelaxed structures. In the insets of Figures 5.10(a-d), we also show the calculated STM topography. The LDOS in Figure 5.10(a) suggests that in this scenario the highest VB is highly localised at the AA' sites, contrary to the experimental findings of Figure 5.8. Interestingly, the highest VB is localised on the B^{S/S} site when no atomic relaxations are included and the layers remain flat, see Figure 5.10(d). This suggests that atomic relaxations in the experimental sample are not as strong as in a free-standing system. Possible origins of this discrepancy include (i) the influence of the substrate which is not included in our simulations, (ii) atomic motions due to thermal fluctuations, and (iii) extrinsic strains. To test this hypothesis, we carry out DFT calculations for twisted bilayers in which the displacements of all atoms from their unrelaxed positions are reduced by a factor of two in Figure 5.10(b) and by a factor of four in Figure 5.10(c), compared to their values in the fully relaxed free-standing system. In Figure 5.10(d) we show the calculation in the absence of relaxation. In these systems, the LDOS in the AA' and the B^{S/S} regions are almost the same near the VB onset in good agreement with the experimental findings. These results clearly demonstrate the high sensitivity of the electronic structure on atomic relaxations.

Figures 5.10(e-h) demonstrate that the wavefunction of the highest lying VB does not correspond to the experimental measurement for the feature V₁ shown in the lower panel of Figure 5.8: the wavefunctions do not form a honeycomb shape, but a triangular pattern. The only exception corresponds to the wavefunctions obtained when all displacements are reduced by a factor of four, see Figure 5.10(g). However, in this case, the dark regions of

the honeycomb pattern are not associated with $B^{S/S}$ regions as in the experiment. Instead, we have found that deeper-lying VBs, whose LDOS are shown in Figure 5.10(i-l), have a low intensity on the $B^{S/S}$ regions when relaxations are absent or strongly reduced, as shown in Figure panels 5.10(k) and (l). This state also exhibits a six-fold symmetry around these $B^{S/S}$ sites as does the honeycomb pattern observed in experiments. We, therefore, assign the experimental maps of the feature V_1 to this deeper-lying VB. Considering the thermal broadening in this experiment, it is not surprising that the contributions from a single narrow flat band would not be the only ones measured at a particular energy.

5.2.3 Conclusion

In conclusion, we use scanning tunneling microscopy and spectroscopy to characterize the spatial distribution of the wave functions corresponding to flat bands in a bilayer WS_2 sample twisted $\approx 3^\circ$ off the antiparallel alignment. To understand the localization at the different high-symmetry stacking regions we performed DFT calculations which revealed that atomic relaxations play a critical role in determining the degree to which the wave functions associated with flat bands localise on the high-symmetry regions. We find that in our samples the atomic relaxations are much suppressed compared to calculations for the idealized system of a bilayer in vacuum. These findings provide insight into the spatial distributions of the wave functions associated with flat bands believed to be responsible for the occurrence of correlated electron phenomena, demonstrating that atomic relaxations are a way to control the localization of the wave functions.

5.2.4 Experimental methods

The sample was prepared by the dry transfer method. Two monolayers of WS_2 (purchased from HQ Graphene) were stacked on each other using the tear-and-stack technique [140, 171]. Graphene (purchased from Graphenea) was used as a substrate to al-

low a sufficiently conductive contact for STM measurements. Both WS_2 and graphite crystals were mechanically exfoliated onto Si/SiO_2 substrates. Monolayer WS_2 was identified optically, and the thickness was confirmed with atomic force microscopy (AFM). Suitable graphite flakes were identified and were picked up with a polydimethylsiloxane (PDMS) stamp covered with polypropylene carbonate (PPC) film on a glass slide. The graphite on the polymer stamp was then used to pick up monolayer WS_2 . The two layers of WS_2 correspond to two halves of a large flake, allowing for precise rotational control. The PPC film was then cut and the 2D material stack was transferred onto a Si/SiO_2 substrate coated with Ti/Au ($5\text{nm}/150\text{nm}$). The sample was then annealed under ultra-high vacuum at 300°C for several hours. The surface was cleaned using an AFM tip [172, 173]. STM measurements were performed at pressures below 10^{-9} Torr, at RT. For STS we used bias modulation of 5.0mV , 1.325kHz and a typical set-point: $V_b = -1.3\text{V}$, $I_T = 150\text{pA}$.

5.2.5 Computational details

This work was performed by Indrajit Maity and Johannes Lischner.

Atomic reconstructions

The twisted bilayer of WS_2 has been generated using the TWISTER package [189]. The total number of atoms in the unit cell of 56.86° twisted bilayer WS_2 is 1986. All the atomic relaxations are performed using classical interatomic potentials fitted to DFT calculations. The intralayer interactions within WS_2 are described using a Stillinger-Weber potential [190], and the interlayer interactions are captured using a Kolmogorov-Crespi potential [191]. All the simulations with classical interatomic potentials are performed using the LAMMPS package [192]. We relax the atoms within a fixed simulation box with a force tolerance of $10^{-6}\text{eV}/\text{\AA}$ for any atom along any direction.

Electronic structure calculations

All the electronic structure calculations were performed using the SIESTA package [193]. All the calculations included spin-orbit coupling [194]. We used Troullier-Martins pseudopotential [195] and the local density approximation with the Perdew–Zunger parametrization as the exchange-correlation functional [196]. We used a double- ζ plus polarization basis for the expansion of wavefunctions. For the electronic structure calculations we used the Γ point in the moiré BZ to obtain the converged ground state charge density. A large vacuum spacing of 20 Å was used in the out-of-plane direction.

Density of states calculations

To obtain well-converged results, the DOS calculations were performed on a fine $5 \times 5 \times 1$ k-grid in the moiré BZ (which corresponds to a $91 \times 91 \times 1$ k-grid of the monolayer BZ). We used a Gaussian with a width of 30meV to represent the δ -function in the DOS calculations.

Local density of states calculations

To obtain the LDOS for selected stackings, we used a $5 \times 5 \times 1$ k-grid to sample the moiré BZ. Furthermore, we average the LDOS over a 9 Å radius in-plane circular patch around the centre of the selected high-symmetry stackings.

Scanning tunneling microscope topography calculations

The calculations associated with the STM topography were performed only using the Γ point in the moiré BZ. Furthermore, we used a Voronoi diagram to coarse-grain atomistic details in the topography.

5.3 Outlook

L. Molino, et al. *Nano Lett.* 23, 24, 11778-11784 (2023) is part of a series of STM papers [34–38, 78–89, 91, 164, 184–186, 197–201] that examine a particular bilayer TMD system at a particular twist and contribute to the understanding of twisted bilayer TMDs in general by filling out the experimental parameter space and examining the role of a specific factor on the band structures: in this case the out-of-plane relaxation. However, interest is now shifting to further exploration of the many-body physics predicted to be produced by flat bands, in particular for quantum simulator applications [34, 105, 181, 187].

Quantum simulation

A quantum simulator is a device that uses actual quantum effects to simulate a model system. With the prospect for control over moiré potential depth, inter-site Coloumb interaction, flat-band energies, number, and bandwidth, and perhaps lattice geometry, offered by the sensitivity of twisted TMDs to twist angle, there is interest in using the periodic moiré potentials in twisted TMDs as quantum simulators of atomic lattices. A quantum simulation of a lattice is of particular interest to realise the Hubbard model: a simple model for crystalline solids that is nonetheless difficult to solve beyond the 1D case [34, 105, 106]. The Hubbard model is thought to capture different correlated phenomena depending on the filling factor, including high-temperature superconductivity and magnetic insulating states [202–207].

Correlated phenomena by definition will be sensitive to the system filling-factor. In an STM experiment, the sample surface must (in general) be exposed, therefore the filling factor must be adjusted with a backgate. In typical experiments on TMD bilayers, the bilayers are placed on a conductive substrate, typically graphite, to allow for sufficiently low in-plane resistance for maintaining feedback [83, 86, 87]. However, a conductive substrate will screen the backgate, therefore a dielectric substrate is necessary, typically hexagonal

BN (hBN), presenting an experimental challenge. Furthermore, correlated phenomena are very sensitive to perturbation from the tip and cannot generally be observed with STM without being disturbed.

H. Li et al. have presented solutions to these problems in a series of papers. Both problems can be solved through the use of a sensing layer, in which the twisted bilayer is encapsulated by graphene on few-layer hBN [35, 36]. In this case, the electronic phenomena in the TMD can be observed indirectly through their influence on the sensing layer. This however limits the spatial resolution to $\sim 5nm$. In other works, they have encapsulated their samples with graphene nano-ribbons [34, 37, 38]. Measurements can be taken in the gaps between the ribbons, where the short path to the graphene for carries keeps in-plane resistance sufficiently low. Efforts to emulate this sample design are reported in Section 3.3. This sample design is paired with a measurement technique in which the tip chemical potential is aligned with the TMD bandgap, and the bias is selected to align the tip and TMD vacuum energies, resulting in reduced tip-sample electric fields and minimizing perturbation [37].

In these works, generalized Wigner crystals in TMD homobilayer and heterobilayer moiré patterns at fractional filling have been observed [34–38], as well as local melting of the crystal as the "density" is increased, resulting in a mixed phase [38]. Furthermore, Wigner "molecules" in which multiple carriers on a single moiré site form an ordered structure have also been observed [37].

These works represent early results in the moiré quantum simulator space; no published works have yet made an effort to systematically exploit the tunability of TMD moiré systems. This may be due to fabrication challenges: no other groups have emulated the techniques outlined by H. Li et al., though the work described in Section 3.3 is near to realising a similar device architecture. Any systematic effort, however, will require higher yield fabrication

processes.

Chapter 6

Charge density waves and interlayer dimerization in 1T-Tantalum Disulfide

The previous chapters have discussed how a periodic superstructure (moiré pattern) emerges in bilayers of transition metal dichalcogenides (TMDs) and can produce dispersionless bands with enhanced electron-electron interactions. In this chapter, we see the reverse phenomenon; electron-electron interactions leading to the emergence of a superstructure (periodic lattice distortion) with bilayer dimerization in a bulk TMD.

The topic of this chapter is the commensurate charge density wave (C-CDW) phase in 1T-TaS₂. This chapter discusses results and reproduces figures from **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". *ACS Nano* 17, 16, 15883–15892 (2023).** This work uses Raman spectroscopy, with the support of reflectance contrast and scanning tunneling microscopy/spectroscopy (STM/STS), to argue that the C-CDW phase in 1T-TaS₂ features a double layer dimerized stacking configuration, and that interlayer interactions play a role in determining its electronic properties. Furthermore, it presents evidence for selective electron-phonon coupling in this system. While the Raman

spectroscopy, reflectance contrast, and data interpretation (including Figure 6.1) were performed by other authors, the STM/STS data presented here was collected and analysed by Laurent Molino with the assistance of Ryan Plumadore and advice of Adina Luican-Mayer.

6.1 Charge density waves

First predicted in the 1930s [109–111, 208, 209], a CDW is a long-range electronic ordering, typically in one-dimensional atomic chains and two-dimensional (2D) crystals [210, 211]. A CDW consists of a static, periodic modulation of the valence electrons, akin to a standing wave, at some wavelength greater than the atomic unit cell size, accompanied by a periodic distortion of the atomic lattice (PLD). CDWs can either be commensurate or non-commensurate. A C-CDW is defined as having a unit cell which is an integer multiple of the atomic lattice unit cell, such that the CDW is always in phase with the lattice.

The formation of a CDW is a Fermi-surface driven process [110, 111, 210]. In the simplest picture, the PLD results in the formation of a mini Brillouin zone (BZ) (akin to a moiré pattern). The enhancement of electron-electron interactions at the BZ edge allows for a net decrease in the energy of the valence electrons. If this energy decrease is greater than the energy cost of straining the lattice to produce a PDL, a CDW can form. This process requires a high degree of electron-phonon coupling since the energy of the valence electrons results in a displacement of the ions of the atomic lattice [107].

In transition metal dichalcogenides

The first experimental observation of a CDW in 2D was in 1T-TaSe₂ [107, 108], and they have since been observed in numerous TMDs including 2H-TaSe₂, 1T-TiSe₂, 1T-VSe₂, and 1T-TaS₂ [108, 115]. 1T-TaS₂ in particular has been extensively studied, in part due to its superconducting phase and multiple phase transitions [108, 114–118, 212–233].

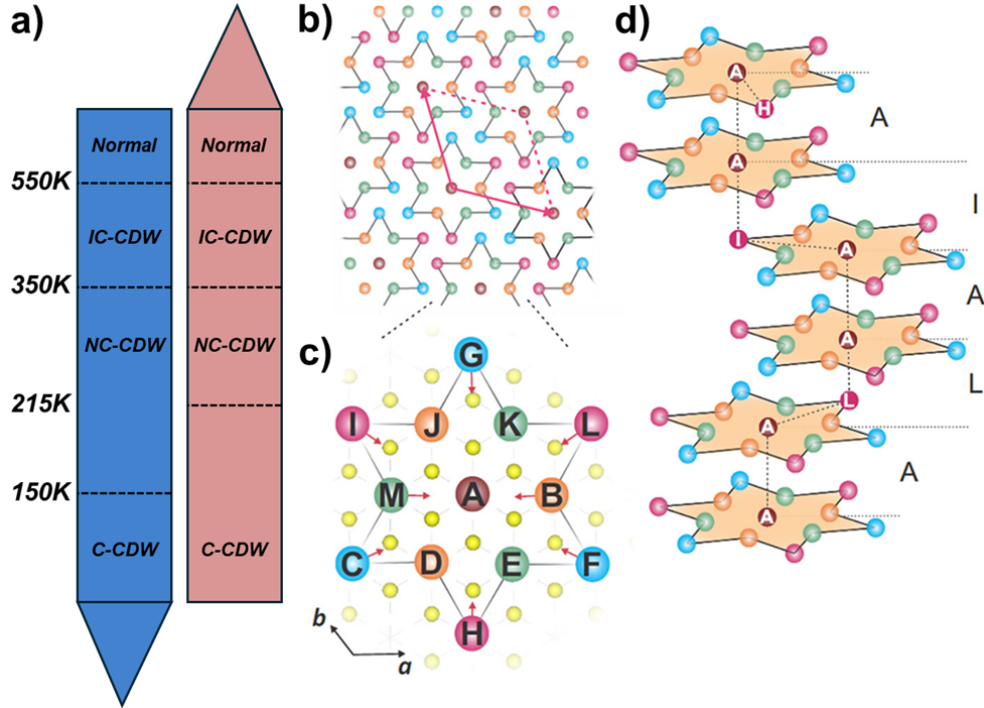


Figure 6.1: Structure and phases of 1T-TaS₂ **(a)** Phase diagram upon cooling and heating. **(b)** Schematic of a supercell for the C-CDW 1T-TaS₂ crystal in the TaTa plane viewed from the top. The parallelogram is the $13a \times 13a$ -superlattice cell of the star-of-David structure. The different hues represent the Ta ions at different sites. **(c)** Labels for the 13 Ta sites (AM) of the star-of-David pattern in the C-CDW phase formed by inward displacements of 12 Ta ions (red arrows). The small yellow ions represent the S atoms. **(d)** Schematic of the double-layer stacking order showing the A, L, A, L, and A stacking sequence, from the bottom to the top.

Upon cooling, 1T-TaS₂ undergoes a series of phase changes [108, 113, 212, 234–236], as shown in Figure 6.1(a). 1T-TaS₂ transitions to an incommensurate CDW (IC-CDW) at $\sim 550K$, and to a nearly commensurate CDW (NC-CDW) at $\sim 350K$. Below $\sim 180K$, it forms a fully commensurate CDW, with a "star of David" structure consisting of 13 transition metal atoms, as shown in Figure 6.1(b) and (c). This structure has been observed experimentally, in particular with STM [114–118]. Several reports of STS on this structure also exist, with maximum energy ranges of $-1500mV$ to $1500mV$ [114], though $-500mV$ to $500mV$, is more typical [116–118]. These works also reported a novel mosaic

phase induced by tip pulsing [118], negative differential resistance [114], and preliminary evidence for layer dimerization [117].

6.2 Selective electron-phonon coupling and interlayer dimerization in 1T-tantalum disulfide

C-CDW 1T-TaS₂ features a metallic-insulator transition that can be triggered by pressure [212, 213], electrostatic doping [214, 215], electric current [219], and laser pulse irradiation [216]. While it has been proposed that the insulating state arises from Mott physics [237–240], recent theoretical work has suggested that interlayer hybridisation is the primary cause [223, 241]. In this case, the insulating ground state corresponds to dimerization of pairs layers with A-type stacking along the c-axis, (as shown in Figure 6.1(d)), with H-, I-, or L-stacking between dimers. A metastable metallic state with no dimerization is proposed to exist at nearly degenerate energy, such that a transition between the two states can be easily induced. Previous Raman work on this system has considered either trigonal symmetric stacking, or disordered stacking in which interlayer interactions are not considered. In **S. Ramos et al. *ACS Nano* 17, 16, 15883–15892 (2023)** [113], Raman work is performed considering a dimerized structure for the first time.

Raman active modes are vibrational modes of a crystal that cause a change in the crystal's polarizability. The number of modes depends on the crystal's symmetry. Group theory predicts that a disordered stacking of monolayers should have 38 Raman active modes, while ordered A-, L- and AL-stacking should have 38, 117, and 234 modes respectively. A dimerized structure is predicted to have 78 Raman active modes. S. Ramos et al. observed at least 58 distinct Raman peaks, however, some of these peaks feature depolarisation ratios that do not correspond to the expected available symmetries, suggesting that several of the peaks are actually convolutions of more than one distinct feature, accounting for the

difference between the 58 observed features and the 78 modes expected in a dimerized structure.

The observed Raman modes are also shown to exhibit an intensity dependence on the excitation energy, with three resonances, at 1.94eV , 2.39eV , and 2.74eV . This result suggests a resonant Raman process with selective electron-phonon coupling.

6.2.1 Scanning tunneling microscopy measurements

Further evidence for a resonant Raman process can be derived from STS measurements. As shown in [242, 243], resonant Raman involves the interaction of a phonon with an exciton. The signatures of the electron-phonon resonance can be observed as a pair of peaks in the STS. However, the observed resonant energies imply that the resonant transitions occur to and/or from energies far from the Fermi level. Most existing STS spectra for C-CDW 1T-TaS₂ were not performed over a broad enough energy range to observe these features [116–118]. It was therefore necessary to conduct STS measurements over a broader energy range.

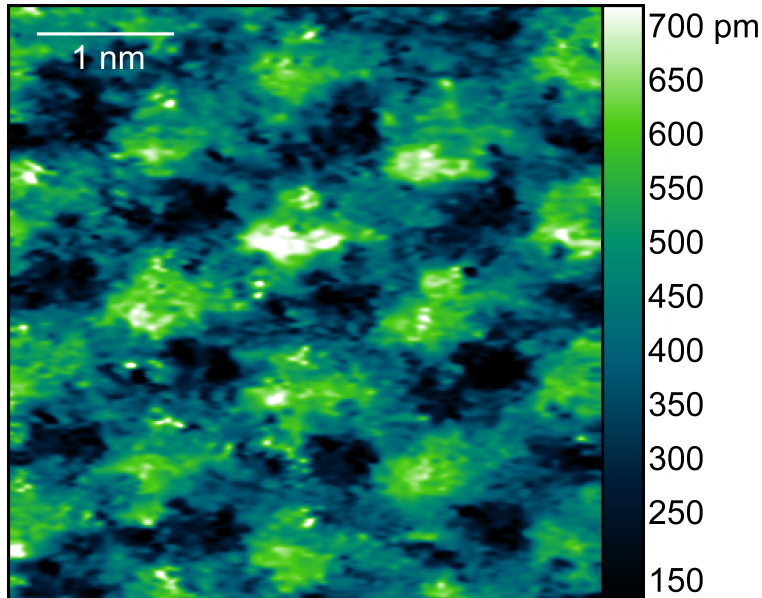


Figure 6.2: STM topography of the C-CDW phase of 1T-TaS₂.

STM measurements were conducted on a freshly cleaved surface of 1T-TaS₂ at a temperature of 13K and a pressure of $\sim 10^{-9} \text{ Torr}$, well within the C-CDW phase. Under these conditions, an STM topography map was taken as shown in Figure 6.2. While the atoms are not resolved, a CDW modulation of the surface topography can be observed. The period of the CDW was measured to be $1.21 \pm 0.05 \text{ nm}$, in agreement with previous work [114, 117].

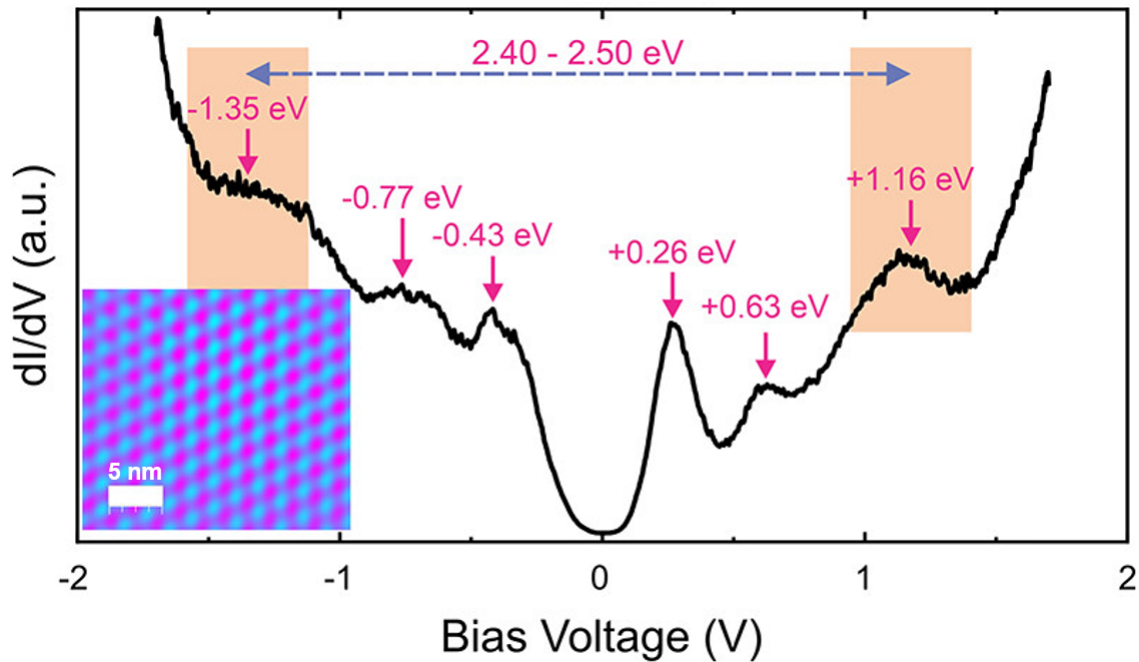


Figure 6.3: STS on the C-CDW phase of 1T-TaS₂. **Inset:** STM topography of charge density wave.

After imaging the C-CDW phase, STS measurements were then taken, as shown in Figure 6.3. In order to resolve the six observed features, it was necessary to finely tune the STM settings. Broad spectrum STS measurements require optimizing for the stability of the tunneling junction while keeping the tunneling current sufficiently low that it does not saturate in the deep valence band (VB) and conduction band (CB). Even with optimal settings, the majority of curves featured saturation or discontinuities, and had to be removed from the data set. Ultimately, greater than 2000 individual spectra were taken. The chal-

lenges described here may be why broad spectrum STS on this system is limited in the literature.

The spectrum presented in Figure 6.3 represents an average of 300 clean curves acquired using a junction with tip-sample distance set at $V_B = 450mV$ and $I_T = 255pA$. A transition of about $2.4 - 2.5eV$ can be seen between the two deepest features in the VB and CB in the density of states, consistent with the prominent $2.4eV$ transition from the optical results.

6.3 Conclusion

In conclusion, the Raman modes newly resolved by [113], along with their anomalous depolarisation ratios, have provided new evidence of interlayer dimerization in C-CDW phase 1T-TaS₂. This result provides experimental validation to theoretical work on this system, supporting the conclusion that interlayer coupling is the origin of its insulating phase, and the observed metal-insulator transition arises from a change in the coupling. Furthermore, this system has been observed to feature a resonant process upon Raman measurement, owing to the presence of selective electron-phonon resonance. This conclusion is supported by the observation of the peaks associated with the most prominent exciton transition with STS. Further work is necessary to determine the nature of this resonance and its relationship with correlated phenomena in this system.

Chapter 7

Conclusion

In this work, scanning tunneling microscopy (STM) and spectroscopy (STS) was used to study superstructures emergent from interlayer interaction in transition metal dichalcogenides (TMDs). A procedure was developed to fabricate twisted TMD samples compatible with STM measurement. Using this method, a series of twisted bilayer WS_2 samples were prepared, hosting moiré superlattices. These samples were used to characterise the structural and electronic properties of the moiré pattern over a range of twist angles and reconstruction regimes.

In Chapter 4, the structural properties of twisted bilayer TMDs were examined, with a discussion of in- and out-of-plane relaxation effects. We observed stacking order domains arising from in-plane reconstruction and featuring interfacial ferroelectricity. We demonstrated local control over the domain walls through the interaction of the domain dipole moments and the electric field from the scanning tip. We then explored the role of anisotropic strain on the shape of the domain wall network, and showed how it can be exploited to produce a complete switching of the local stacking order at experimentally accessible fields.

In Chapter 5, we then examined the electronic properties of twisted bilayer TMDs, with a focus on the emergence of flat bands. In another twisted WS_2 sample, we observed density of states spectra that are compatible with the presence of flat-bands. By examining the

spatial distribution of the wavefunction on the valence band edge, and through comparison to first principles work, we investigated the role of out-of-plane relaxation in the localisation of the flat band wavefunctions. We present evidence that in our sample moiré buckling is suppressed by the substrate, leading to disagreement with standard first-principles techniques. These results are a warning against over reliance on density functional theory techniques that do not take into account the substrate effects for understanding twisted TMD (tTMD) systems.

The lessons learned through these works can be applied to the fabrication and measurement of electrostatically doped tTMD samples for quantum simulation applications. Progress toward this goal was presented in Section 3.3.

In Chapter 6, additional work was also presented on the commensurate charge density wave in 1T-TaS₂. Here, STM was used to support the argument for interlayer dimerization and selective electron-phonon coupling in this system. This work demonstrates another case of the emergence of new phases of matter through a superstructure in TMDs.

Outlook

Through the research presented and referenced in Chapters 4 and 5, the community has now developed an understanding of the structural and electronic properties of twisted bilayer TMDs. In the future, this knowledge can be applied to fundamental research on increasingly complex systems, as well as device applications, including quantum simulators. However, several challenges must be overcome.

As discussed in Chapter 4, the ferroelectric switching present in parallel-aligned bilayer TMDs is of interest for electronic device applications, in particular memristors [2, 3, 149], a non-linear electrical component which acts as a combined switch and memory unit. However, to understand how this system would behave as a switch or memory unit, it is necessary to better understand the hysteretical and memory effects of the domain wall bending.

While preliminary work has begun [145], a more thorough characterisation of the behavior of this system in potential device architectures is necessary.

The most critical barrier in two-dimensional (2D) materials for both fundamental research and device application is the challenge associated with heterostructure fabrication. Commercial application and systematic research efforts would both require high-yield fabrication processes that can produce clean, uniform, complex heterostructures with a high degree of twist angle control, and, potentially, large area samples with reproducible shapes. Progress in this direction can be divided into three complementary research efforts: higher yield transfer techniques, better growth techniques, and automation.

The dry transfer technique is broadly used for fabricating 2D materials heterostructures [34–36, 38, 81, 82, 84, 87, 89–91, 93, 95, 130, 134, 141, 143, 146, 150, 153–155, 244–253]. Current efforts at developing better dry transfer techniques include modifying materials and procedures to improve yield and twist angle control [254, 255]. As an alternative to dry transfer, many scanning probe studies of 2D materials use heterostructures grown layer-by-layer, using techniques such as chemical vapor deposition, metal organic chemical vapor deposition, and molecular beam epitaxy [78, 79, 164, 184, 185, 198–200, 256–276]. Improvement in defect rate and grain size, as well as the prospect for tunable-period grown moiré patterns, may make these techniques an appealing alternative in the future. Finally, a few examples of entirely automated transfer apparatuses, complete with characterisation, now exist [277, 278], presenting an opportunity for high throughput experimentation.

Progress on the fabrication of 2D materials in general would have important implications for tTMDs in particular. As we saw in Chapter 5, bilayer tTMDs of different materials, twisted at different twist angles, will feature a variety of moiré periods, moiré potential depths, and through reconstruction, moiré potential geometries. These factors in turn control the num-

ber, energies, and bandwidth of the flatbands, the geometry of their wavefunctions, and strength of the inter-site Coloumb interaction, making for highly tunable lattice quantum simulators if sufficient control can be achieved [34, 105, 181, 187]. The full potential of these systems to simulate models such as the Hubbard model can only be realised through large quantities of finely controlled, reproducible samples. However, preliminary work on less controlled quantum simulator systems continues to be necessary, even as fabrication methods are being developed, to demonstrate the device's capabilities and refine measurement techniques. In particular, work on multilayer twisted samples may yield even more degrees of freedom that would be of interest for quantum simulators, including going beyond the hexagonal lattice geometry [94, 155, 156].

In Chapter 1, we place the research on bilayer TMDs in the context of the broader 2D material field. In particular, we saw how work on TMDs builds on work on magic-angle twisted bilayer graphene (MATBG). Since the discovery of MATBG, the complexity of the graphene heterostructures under investigation has increased, with many examples of multilayer systems in the literature [62, 82, 279, 280]. Research on TMDs will likely also follow this path, especially as improved fabrication techniques make increasingly complex sample architectures feasible.

In summary, moiré patterns and other superstructures emerge in systems of 2D materials through interlayer interactions, leading to multilayer structures that are greater than the sum of their parts. This thesis represent a contribution to the understanding of the structural and electronic properties of these systems, moving the field forward toward device application and a deeper knowledge of 2D material physics.

Chapter 8

Appendices

8.1 Moiré simulator code

In this section, software is presented to simulate a moiré pattern for arbitrary lattices and twist angles. For bilayers of hexagonal atomic lattices the periodicity of the emergent moiré superlattice is straightforward (Equation 1.1). However, moiré patterns formed from multi-layer or mixed symmetry heterostructures can be more complex. An example of a mixed symmetry heterostructure is presented in Ref. [247]. In this case, a moiré pattern is formed between graphene, which has a hexagonal unit cell, and ReS₂, which is triclinic. The emergent moiré pattern features multiple periodic orders which vary differently with twist angle, with the most prominent being a striped phase with a maximum period at $\sim 12^\circ$. When studying mixed symmetry systems such as this one, it can be helpful to simulate the moiré pattern as it might be observed with scanning tunneling microscopy (STM).

The code presented below is a moiré pattern simulator. Each layer is constructed by defining a lattice with a basis. A two-dimensional array of "intensities" for each layer's unit cell is populated by placing a Gaussian of chosen width at each atom site. The unit cell is then multiplied to produce a lattice of the desired extent at the desired angle. The layers are all then superimposed, to produce a figure analogous to what might be observed with STM. In Figure 8.1, it is demonstrated how the code can be used to simulate the striped

phase in 12° twisted graphene/ReS₂. Note that this program does not consider relaxation effects. In Section 8.1, an example of the code implemented for twisted bilayer graphene is given.

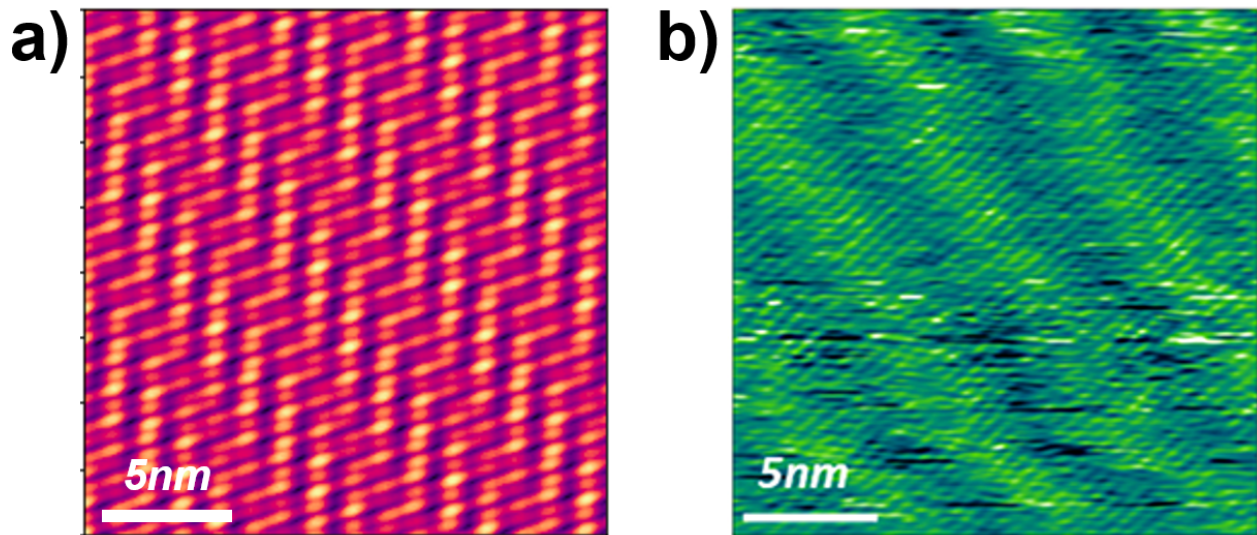


Figure 8.1: (a) STM topography map compared to (b) simulation of 12° twisted graphene/ReS₂ moiré pattern.

Moiré simulator python code

```

1  """
2  Models moire pattern formed between two lattices
3  """
4  import numpy as np
5  import matplotlib.pyplot as plt
6
7  #twists set of lattice vectors by angle theta
8  def twist_lvs(lvs, theta_rad):
9      t_lvs = np.zeros(shape=(2,2))
10     R = np.array([[np.cos(theta_rad), -np.sin(theta_rad)], [np.sin(
11         theta_rad), np.cos(theta_rad)]])
12     t_lvs[0,:] = np.dot(R, lvs[0,:])
13     t_lvs[1,:] = np.dot(R, lvs[1,:])
14     return t_lvs
15
16 #creates 2x2 array of lattice vectors
17 def make_lvs(a, b, gamma_deg, theta_deg):
18     gamma_rad = gamma_deg * np.pi/180
19     theta_rad = theta_deg * np.pi/180
20     lvs = np.zeros(shape=(2,2))
21     lvs[0,0] = a
22     lvs[1,0] = b * np.cos(gamma_rad)
23     lvs[1,1] = b * np.sin(gamma_rad)

```

```

23     t_lvs = twist_lvs(lvs, theta_rad)
24     return t_lvs
25
26 #converts point from reduced-coordinates to cartesian coordinates
27 def rc_to_cc(rc_point, lvs):
28     cc_point = np.zeros(shape=2)
29     for i in [0,1]:
30         for j in [0,1]:
31             cc_point[i] += rc_point[j] * lvs[j,i]
32     return cc_point
33
34 #converts point from cartisian-coordinates to reduced-coordinates
35 #based on general case https://en.wikipedia.org/wiki/
36 #need to add dummy lattice vector in third dimension
37 def cc_to_rc(cc_point_2d, lvs, mod=np.inf):
38     #convert everything to 3d
39     cc_point_3d = np.zeros(shape=3)
40     cc_point_3d[0:2] = cc_point_2d
41     lvs_3d = np.zeros(shape=[3,3])
42     lvs_3d[0:2,0:2] = lvs
43     lvs_3d[2,2] = 1
44     #initialize local variables
45     rc_point_2d = np.zeros(shape=2)
46     rc_point_3d = np.zeros(shape=3)
47     face_areas = np.zeros(shape=(3,3))
48     #do math
49     for i in range(0,3):
50         face_areas[i][:] = np.cross(lvs_3d[(i+1)%3][:], lvs_3d[(i+2)
51 %3][:])
52     cell_vol = np.dot(lvs_3d[0][:], face_areas[0][:])
53     for j in range(0,3):
54         rc_point_3d[j] = np.dot(cc_point_3d, face_areas[j][:]) / cell_vol
55     #return to 2d, apply modulo
56     rc_point_2d = rc_point_3d[0:2]%mod
57     return rc_point_2d
58
59 #calculates distances between point a and b, which are two element vectors
60 def get_dist(a, b):
61     d2 = 0
62     for i in range(0,2):
63         d2 += (b[i] - a[i])**2
64     d = np.sqrt(d2)
65     return d
66
67 #get value of gaussian of given std with x=dist
68 def gaussian(dist, std):
69     val = 1.0/(std * np.sqrt(2*np.pi)) * np.exp(-1.0/2.0 * (dist /std)**2)
70     return val
71
72 #makes a list of atoms that atom_range steps away the central unit cell
73 def make_atom_list(atom_range, lvs):
74     atom_list = []
75     for i in range(-atom_range, atom_range + 2):
76         for j in range(-atom_range, atom_range + 2):
77             atom = rc_to_cc([i,j], lvs)
78             atom_list.append(atom)

```

```

78     return atom_list
79
80 #normalizes 2d array, assumes data is all positive
81 def norm(data):
82     dims = list(np.shape(data))
83     norm_data = np.zeros(shape=dims)
84     max_val = np.max(data)
85     for i in range(0, dims[0]):
86         for j in range(0, dims[1]):
87             norm_data[i,j] = data[i,j] / max_val
88     return norm_data
89
90 #creates a square array representing one unit cell in reduced co-ordinates
91 #values of 2 seem to work fine for atom_range and res_factor
92 #Call gaussian for atom shape by default, could use different shape
93 def make_uc_square(lvs, res, atom_range=2, res_factor=2, atom_func=
    gaussian, atom_size=0.1):
94     #initialize parameters
95     lvs_lengths = [get_dist([0,0],lvs[0,:]), get_dist([0,0],lvs[1,:])]
96     square_size = max(lvs_lengths)*res*res_factor
97     square_size = int(square_size)
98     pixel_size_rc = 1.0/square_size
99     uc_square = np.zeros(shape=[square_size,square_size])
100     #fill in square
101     atom_list = make_atom_list(atom_range, lvs)
102     for x in range(0, square_size):
103         for y in range(0, square_size):
104             point_val = 0
105             rc_point = np.array([x*pixel_size_rc, y*pixel_size_rc])
106             cc_point = rc_to_cc(rc_point, lvs)
107             for atom in atom_list:
108                 atom_dist = get_dist(cc_point, atom)
109                 point_val += atom_func(atom_dist, atom_size)
110                 uc_square[x,y] = point_val
111     #normalises array
112     uc_norm = norm(uc_square)
113     return uc_norm
114
115 #makes lattice from lvs with one atom basis
116 #for each point in the lattice array, it converts the point to rc mod 1,
117 #and find the appropriate value from uc_square
118 #shifts lattice by shift, a vector in rc
119 def make_sub_lattice(uc_square, lvs, res, size, shift):
120     n_points = int(size*res)
121     uc_dim = uc_square.shape[0]
122     sub_lat_data = np.zeros(shape=[n_points,n_points])
123     for i in range(0, n_points):
124         for j in range(0, n_points):
125             cc_point = [i/res - shift[0], j/res - shift[1]]
126             rc_point = cc_to_rc(cc_point, lvs, mod=0.999999999) #should
127             #be able to just be mod=1, not sure why not working
128             uc_point = rc_point * uc_dim
129             sub_lat_data[i,j] = uc_square[int(np.floor(uc_point[0])), int
130             (np.floor(uc_point[1]))]
131     return sub_lat_data
132
133 #plots data as a colour plot
134 #need each figure to have a different n_fig, otherwise issues arise
135 def plot(data, size, n_fig):

```

```

134     rot_data = np.rot90(np.fliplr(data))
135     plot_extent = (0, size, 0, size)
136     plt.figure(n_fig)
137     plt.contourf(rot_data, cmap='magma', levels = 100, extent=plot_extent)
138     plt.axis('scaled')
139     cbar = plt.colorbar()
140     plt.xlabel("x (nm)")
141     plt.ylabel("y (nm)")
142     cbar.set_label('', rotation=270)
143     cbar.set_ticks([])
144     plt.autoscale(enable=True)
145
146     #make a lattice with a basis
147     #a = lattice_vector_1 length
148     #b = lattice_vector_2 length
149     #gamma_deg = angle between a and b in degrees
150     #theta_deg = twist of entire lattice in degrees
151     #basis = a 2D array of basis vectors
152     #trans = translation of entire lattice, [x,y]
153     #atom_sizes = a list of atoms sizes (atom gaussian std), need same number
154     #               of entries as there are basis vectors
155     #size = size of lattice in nm
156     #res = number of pixels per nm
157     #plot_all = if true, plots UC square, sublattices, and final lattice
158     def make_lattice(a, b, gamma_deg, theta_deg, basis, trans, atom_sizes,
159                     size, res, plot_all=False):
160         n_points = int(size*res)
161         lat_data = np.zeros(shape=[n_points,n_points])
162         n_basis = basis.shape[0]
163         for i in range(0, n_basis):
164             lvs = make_lvs(a, b, gamma_deg, theta_deg)
165             uc_square = make_uc_square(lvs, res, atom_range=2, res_factor=2,
166                                     atom_func=gaussian, atom_size=atom_sizes[i])
167             shift = trans
168             for j in [0,1]:
169                 shift += basis[i,j] * lvs[j,:]
170             sub_lat = make_sub_lattice(uc_square, lvs, res, size, shift)
171             lat_data += sub_lat
172             if plot_all == True:
173                 plot(uc_square, 1, i + 2) #trying to never have the same
174                 figure number
175                 plot(sub_lat, size, i + n_basis + 3)
176                 norm_lat_data = norm(lat_data)
177                 if plot_all == True:
178                     plot(norm_lat_data, size, 1)
179                 return norm_lat_data
180
181     #Example: Bilayer Graphene with a 15 deg twist
182     #Lattice 1
183     a = 0.246
184     b = 0.246
185     gamma_deg = 120
186     theta_1 = 0
187     trans_1 = [0,0]
188     basis = np.array([[0.,0.], [0.3333333333, 0.6666666667]])
189     atom_sizes = [0.05, 0.05]
190     size = 4
191     res = 100
192     lat_1 = make_lattice(a, b, gamma_deg, theta_1, basis, trans_1, atom_sizes,

```



```

        size, res, plot_all=True)
189 #Lattice 2 (doesn't plot)
190 #Here we re-use some of our variables from the first lattice, you can only
    do this if the two lattices are the same
191 theta_2 = 15
192 trans_2 = [0,0]
193 lat_2 = make_lattice(a, b, gamma_deg, theta_2, basis, trans_2, atom_sizes,
    size, res, plot_all=False)
194 #Moire
195 moire = lat_1 + lat_2
196 plot(moire, size, 100)

```

8.2 Domain wall model implementation code

The code below is a program for applying the domain wall bending model discussed in Chapter 4 to STM topography maps. After going through basic analysis (background subtraction, row alignment, etc.), STM maps are imported by the program. Domain walls are then manually identified by their vertices, and labeled with their type based on what domain wall model will be applied to them (equilateral triangle, elongated triangle, double domain wall). Model parameters are input, including B , a variable proportional to the displacement field. Multiple values of B can be chosen, and the domain walls are plotted for each, facilitating the manual selection of the best fit.

Tools are built in for facilitating the accurate selection of the domain wall vertices, and correcting improperly selected vertices. Options are present for plotting style.

Domain wall python code

```

1  """
2  Domain Wall Fitter
3
4  Used for visually fitting STM data of domain walls in P-aligned TMD
    homobilayer
5  TMDs in out-of-plane E-field to string-like model, as presented in
6  https://doi.org/10.1002/adma.202207816
7
8  See Work Area on line 360 for detailed use instructions
9  """
10
11 ##### CODE AREA, DO NOT TOUCH #####
12 import numpy as np
13 from scipy.integrate import quad
14 import matplotlib.pyplot as plt
15 from matplotlib_scalebar.scalebar import ScaleBar

```

```

16 import cv2
17 import math
18 from scipy import optimize
19
20 #removes curves of a certain type from vs list
21 def remove_type(n, vs):
22     vs_trimed = np.copy(vs)
23     for i in range(0, len(vs[4,:])):
24         if vs[i,4] == n:
25             vs_trimed = np.delete(vs, i, 0)
26     return vs_trimed
27
28 #returns length of line
29 def get_len(line_vs):
30     x0, y0, x1, y1 = line_vs[0], line_vs[1], line_vs[2], line_vs[3]
31     l = np.sqrt((x1 - x0)**2 + (y1 - y0)**2)
32     return l
33
34 #this is f from the model
35 def f(x, l, A, B):
36     # af^3 + bf^2 + cf +d
37     #[a, b, c, d]
38     roots = np.roots([1, 0, -1*A, -2*B*(x - l/2)])
39     is_real = np.isreal(roots)
40     good_roots = []
41     for i in range(0, len(roots)):
42         if is_real[i] == True and abs(roots[i]) <= 1:
43             good_roots.append(roots[i])
44     if len(good_roots) == 1:
45         return good_roots[0]
46     else:
47         print('ERROR: {0} GOOD ROOTS'.format(len(good_roots)))
48         print(roots)
49
50 def int_arg(x, l, A, B):
51     f_val = f(x, l, A, B)
52     return f_val / np.sqrt(1 - f_val**2)
53
54 #this is F from the model
55 def F(x, l, A, B):
56     return quad(int_arg, 0, x, args=(l,A,B))[0]
57
58 #alpha from model, accounts for iso triangles
59 def shift_curve(Fs, line_vs):
60     x0, y0, x1, y1 = line_vs[0], line_vs[1], line_vs[2], line_vs[3]
61     alpha = np.arctan2(y1 - y0, x1 - x0)
62     new_Fs = np.zeros_like(Fs)
63     new_Fs[:,0] = Fs[:,0] * np.cos(alpha) - Fs[:,1] * np.sin(alpha) + x0
64     new_Fs[:,1] = Fs[:,1] * np.cos(alpha) + Fs[:,0] * np.sin(alpha) + y0
65     return new_Fs
66
67 #generate equilateral triangle domain walls
68 #line vs is vertices
69 #A and B are model parameters
70 #if var_A == True, corrects for misalignment from crystal direction
71 def eql_DW(line_vs, A, B, theta, var_A):
72     if var_A == 'all':
73         theta_rad = theta * 2*np.pi/360
74         line_angle = get_vs_angle(line_vs)

```

```

75     grid_angles = np.ones(7) * theta_rad + np.arange(0,7,1) * 60 *
2*np.pi/360
76     phis = np.ones(7) * line_angle - grid_angles
77     phi = np.amin(abs(phis))
78     A_mod = A + 3*np.cos(phi) - 3
79     else:
80         A_mod = A
81     x0, y0, x1, y1 = line_vs[0], line_vs[1], line_vs[2], line_vs[3]
82     l = np.sqrt((x1 - x0)**2 + (y1 - y0)**2)
83     xs = np.arange(0, l, 0.1)
84     Fs = np.zeros(shape=(len(xs),2))
85     Fs[:,0] = xs
86     for j in range(0, len(xs)):
87         Fs[j,1] = F(Fs[j,0], l, A_mod, B)*np.sign(line_vs[4]) #flips sign
88     trans_Fs = shift_curve(Fs, line_vs)
89     return trans_Fs
90
91 #solve model equation with bisection
92 def bisect(f, bounds, instep=1e-4, error_tol=1e-6):
93     a, b = bounds[0] + instep, bounds[1] - instep
94     assert(f(a) * f(b) < 0)
95     error = abs(a - b)/2.
96     phi = (a + b)/2.
97     count = 0
98     while error > error_tol and count < 1000:
99         if f(a)*f(phi) < 0:
100             b = phi
101         elif f(b)*f(phi) < 0:
102             a = phi
103         else:
104             print('ERROR')
105             phi_new = (a + b)/2.
106             error = abs(phi - phi_new)
107             phi = phi_new
108             count += 1
109     return phi
110
111 #finds angle of line between two points
112 def get_vs_angle(line_vs):
113     rise = line_vs[3] - line_vs[1]
114     run = line_vs[2] - line_vs[0]
115     angle = np.arctan2(rise, run) % (2*np.pi)
116     return angle
117
118 #plots DW for iso triangles, l0 is triangle base
119 #accounts for domain wall merging
120 #here a is alpha, d is delta
121 def iso_DW(l0_vs, l1_vs, l2_vs, A, B, scale, res, pix_cutoff, theta, var_A
):
122     l0, l1, l2 = get_len(l0_vs), get_len(l1_vs), get_len(l2_vs)
123
124     #calculates A_mod
125     if var_A == 'iso' or var_A == 'all':
126         theta_rad = theta * 2*np.pi/360
127         l1_angle = get_vs_angle(l1_vs)
128         grid_angles = np.ones(7) * theta_rad + np.arange(0,7,1) * 60 *
2*np.pi/360
129         phis = np.ones(7) * l1_angle - grid_angles

```

```

130     phi = np.amin(abs(phis))
131     A_mod = A + 3*np.cos(phi)**2 - 3
132 else:
133     phi = 0
134     A_mod = A
135
136 #calculate angles
137 a = np.arccos((l1**2 + l2**2 - l0**2)/(2*l1*l2))
138 a_opt = lambda a1 : ((l1 - np.sqrt(2*l1*A_mod*np.tan(a1)/B)) / (np.
cos(a1)) ) - ((l2 - np.sqrt(2*l2*A_mod*np.tan(a - a1)/B)) / (np.cos(a -
a1)) )
139 a1 = bisect(a_opt, [0, a])
140
141 #calculate other variables
142 l1_star = 2*A_mod*np.tan(a1) / B
143 d1 = (l1 - np.sqrt(l1*l1_star)) * np.heaviside((l1 - l1_star),0)
144 if l1 <= l1_star:
145     x0 = l1/2.0
146 elif l1 > l1_star:
147     x0 = l1 - np.sqrt(l1*l1_star) + l1_star/(2.0)
148 else:
149     print('ERROR with l_star')
150 L1 = d1 / np.cos(a1)
151
152 #plot
153 xs_ddw = np.arange(0, d1, 0.1)
154 xs_crv = np.arange(d1, l1, 0.1)
155 ys_ddw = np.zeros(shape=(len(xs_ddw),2))
156 ys_crv = np.zeros(shape=(len(xs_crv),2))
157 ys_ddw[:,0] = xs_ddw
158 ys_crv[:,0] = xs_crv
159 for i in range(0, len(xs_ddw)):
160     ys_ddw[i,1] = np.tan(a1) * xs_ddw[i] * np.sign(l1_vs[4])
161 for j in range(0, len(xs_crv)):
162     ys_crv[j,1] = (-1*B/(2.0*A_mod)) * (xs_crv[j] - l1) * (xs_crv[
j] - 2*x0 + l1) * np.sign(l1_vs[4])
163 trans_ys_ddw = shift_curve(ys_ddw, l1_vs)
164 trans_ys_crv = shift_curve(ys_crv, l1_vs)
165
166 #calculate L_eff, point at which deviation exceeds resolution
167 res_limit = pix_cutoff*scale/res
168 ys_eff = np.copy(ys_crv)
169 ys_eff[:,1] = abs(ys_eff[:,1] - np.tan(a1) * ys_eff[:,0] * np.sign(
l1_vs[4]))
170 for i in range(0, len(xs_crv)):
171     if ys_eff[i,1] > res_limit:
172         L_eff = ys_eff[i,0]
173         break
174     else:
175         L_eff = 0
176
177 return trans_ys_ddw, trans_ys_crv, l0, L1, L_eff, A_mod, phi
178
179 #manually plots DDWs
180 #don't generally use this
181 def DDW(line_vs):
182     x0, y0, x1, y1 = line_vs[0], line_vs[1], line_vs[2], line_vs[3]
183     return np.array([[x0, y0],[x1, y1]])

```

```

184
185 #expects vs = [[x0, y0, x1, y1, sign], ...]
186 #main function for plotting domain wall, calls on above
187 #if plotting DDW manually, will report comparison of manually selected DDW
    to theory
188 #see paper for comparison details
189 def plot_dw(pic, vs, A, Bs, theta, var_A, suf = '', plot_pic=True,
    plot_points=False, plot_lines=False, plot_grid=False, report=False,
    scale=200, res=128, sb=True, pix_cutoff=1, plot_ddw=False):
190     colors = ['violet', 'white', 'white']
191
192     for B in Bs:
193         fig, ax = plt.subplots()
194         n_lines = len(vs[:,0])
195
196         if plot_grid == True:
197             ax.xaxis.set_ticks(np.arange(0, scale+1, scale/20))
198             ax.yaxis.set_ticks(np.arange(0, scale+1, scale/20))
199             ax.grid()
200         else:
201             ax.xaxis.set_ticks([])
202             ax.yaxis.set_ticks([])
203             ax.spines['top'].set_visible(False)
204             ax.spines['right'].set_visible(False)
205             ax.spines['bottom'].set_visible(False)
206             ax.spines['left'].set_visible(False)
207             ax.title.set_text('{0} \n B = {1}'.format(pic, B))
208             if sb == True:
209                 scalebar = ScaleBar(1, "nm", fixed_value=50, location='
lower right', color='white', box_alpha=0.0, label_loc='top')
210                 ax.add_artist(scalebar)
211
212         if plot_points == True:
213             n_iso = np.count_nonzero(vs[:,4] == 0)
214             noDDW_vs = np.copy(vs[n_iso:,:])
215             ax.plot(noDDW_vs[:,0], noDDW_vs[:,1], marker="o", markersize
=10, color='white', fillstyle='none', linewidth=0)
216             ax.plot(noDDW_vs[:,2], noDDW_vs[:,3], marker="o", markersize
=10, color='white', fillstyle='none', linewidth=0)
217
218         if plot_lines == True:
219             n_iso = np.count_nonzero(vs[:,4] == 0)
220             L_vs_l0 = np.zeros(shape = (2*n_iso, 4))
221             A_mods = np.zeros(shape = (2*n_iso, 2))
222             for i in range(0, n_lines):
223                 line_vs = vs[i,:]
224                 if abs(line_vs[4]) == 0:
225                     Fs = DDW(line_vs)
226                 elif abs(line_vs[4]) == 1:
227
228
229                     l1_vs = vs[i,:]
230                     if (i - n_iso)%2 == 0:
231                         l2_vs = vs[i+1,:]
232                     elif (i - n_iso)%2 == 1:
233                         l2_vs = vs[i-1,:]
234                     l0_index = 3*n_iso + math.floor((i - n_iso)/2.0)
235                     l0_vs = vs[l0_index,:]

```

```

236         Fs_ddw, Fs_curve, l0i, Li_theory, L_eff, A_mod, phi =
237         iso_DW(l0_vs, l1_vs, l2_vs, A, B, scale, res, pix_cutoff, theta, var_A)
238
239         if plot_ddw == True:
240             nL = int((i - n_iso)/2)
241             n1 = int(i - n_iso)
242             L_vs = vs[nL,:]
243             L_exp = get_len(L_vs)
244             L_vs_l0[n1,:] = np.array([l0i, Li_theory, L_exp,
L_eff])
245             A_mods[n1,0:2] = np.array([A_mod, phi*360/(2*np.pi
)])
246
247             ax.plot(Fs_curve[:,0], Fs_curve[:,1], color=colors[abs
(line_vs[4])], linewidth=2)
248             ax.plot(Fs_ddw[:,0], Fs_ddw[:,1], color='red',
linewidth=2)
249
250             elif abs(line_vs[4]) == 2:
251                 Fs = eql_DW(line_vs, A, B, theta, var_A)
252                 ax.plot(Fs[:,0], Fs[:,1], color=colors[abs(line_vs[4])
], linewidth=2)
253
254             else:
255                 print('ERROR: UNDEFINED DW NUMBER')
256
257             if plot_ddw == True:
258                 print('l0, L_theory, L_exp, L_eff:')
259                 print(repr(L_vs_l0))
260                 print()
261                 print('line_vs, A_mod, phi:')
262                 print(repr(A_mods))
263             if plot_pic == True:
264                 im = np.flip(plt.imread(pic), axis=0)
265                 implot = plt.imshow(im, origin='lower', extent=[0,scale,0,
scale])#, extent=[500,500])
266                 plt.savefig('{0}_dwf{1}.png'.format(pic[0:-4], suf), dpi=600,
bbox_inches='tight')
267                 plt.show()
268
269             if report == True:
270                 vs_with_l = np.zeros(shape=(len(vs[:,0]), 3))
271                 vs_with_l[:, 0:2] = vs[:, 4:6]
272                 x0, y0, x1, y1 = vs[:, 0], vs[:, 1], vs[:, 2], vs[:,3]
273                 l = np.sqrt((x1 - x0)**2 + (y1 - y0)**2)
274                 vs_with_l[:,2] = l
275                 name = '{0}_pnts_{1}.txt'.format(pic[0:-4], suf)
276                 np.savetxt(name, vs)
277
278 #select vertices by clicking
279 def click_event(event, x, y, flags, params):
280     if event == cv2.EVENT_LBUTTONDOWN:
281         print(x, ' ', y)
282         font = cv2.FONT_HERSHEY_SIMPLEX
283         cv2.putText(img, str(x) + ', ' +
284                     str(y), (x,y), font,
285                     1, (255, 0, 0), 2)

```

```

286         cv2.imshow('image', img)
287         clicks.append(x)
288         clicks.append(y)
289
290 def clicks_to_vs(clicks, i, n, scale, n_pixels):
291     if len(clicks)%4 != 0:
292         print('ERROR: UNPAIRED VERTICES')
293     else:
294         n_lines = int(len(clicks)/4)
295         vs_points_only = np.reshape(clicks, (n_lines, 4))
296         vs = np.zeros(shape=((n_lines, 6)), dtype=int)
297         vs[:,0:4] = vs_points_only * scale / n_pixels #switchs from
298         default scale to correct scale
299         vs[:,1] = -1 * vs[:,1] + scale #flips y-axis
300         vs[:,3] = -1 * vs[:,3] + scale
301         vs[:,4] = i * np.ones(n_lines)
302         if i == 1: #selects base for iso, assumes you select bases first
303             in eql, in order
304             for j in range(0, n_lines):
305                 vs[j,5] = n + math.floor(j/2.0)
306         return(vs)
307
308 #makes sure domain walls meet by matching points within a threshold radius
309 def match_points(vs, thresh):
310     matched_vs = np.copy(vs)
311     n_lines = np.shape(vs)[0]
312     for i in range(0, n_lines):
313         for j in range(0, 2):
314             point1 = matched_vs[i, 2*j:2*j+2]
315             for k in range(i, n_lines):
316                 for l in range(0, 2):
317                     point2 = matched_vs[k, 2*l:2*l+2]
318                     if np.amax(abs(point1 - point2)) <= thresh:
319                         matched_vs[k, 2*l:2*l+2] = point1
320     return matched_vs
321
322 #shifts points within threshold radius from new point
323 def shift_points(new_points, vs, thresh):
324     matched_vs = np.copy(vs)
325     n_lines = np.shape(vs)[0]
326     for n in range(0, len(new_points)):
327         new_point = new_points[n]
328         for i in range(0, n_lines):
329             for j in range(0, 2):
330                 point = matched_vs[i, 2*j:2*j+2]
331                 if np.amax(abs(new_point - point)) <= thresh:
332                     matched_vs[i, 2*j:2*j+2] = new_point
333     return matched_vs
334
335 #changes order of points in curve
336 def flip_curve(lines, vs, thresh):
337     matched_vs = np.copy(vs)
338     n_lines = np.shape(vs)[0]
339     for n in range(0, len(lines)):
340         point1 = lines[n,0:2]
341         point2 = lines[n,2:4]
342         for i in range(0, n_lines):

```

```

341         point3 = matched_vs[i, 0:2]
342         point4 = matched_vs[i, 2:4]
343         if (np.amax(abs(point1 - point3)) <= thresh and np.amax(abs(
point2 - point4)) <= thresh) or \
344             (np.amax(abs(point1 - point4)) <= thresh and np.amax(abs(
point2 - point4)) <= thresh):
345             matched_vs[i, 4] = matched_vs[i, 4] * -1
346         return matched_vs
347
348 #Changes scale on vertex network
349 def rescale_vs(vs, old_scale, new_scale):
350     scale_factor = int(new_scale)/old_scale
351     new_vs = np.zeros_like(vs)
352     new_vs[:,0:4] = vs[:,0:4] * scale_factor
353     new_vs[:,4:7] = vs[:,4:7]
354     return new_vs
355
356 %%
357 ##### WORKING AREA, MODIFY HERE #####
358
359 #1: Select model parameters
360 #Select and A and B values
361 #A = 3.52 for tWS2
362 #Can input multiple values of B separated by commas, will make image for
each
363 #B typically from 0.005 to 0.02
364 A = 3.52
365 Bs = [0.009]
366
367 #2: Select file name
368 #pic is path to scan file
369 #suffix is appended to scan file name when saving
370 pic = 'STM_topography.png'
371 suffix = '_LM'
372
373 #3: Select scan parameters
374 #scale is scan size in nm
375 #pix_cutoff is error on domain wall position in pixels (used to calculate
DDW length error)
376 #theta is angle of the unstrained network, used to modify A parameter
377 #var_A selects for what domain walls the A parameter is modified
378 scale = 200
379 pix_cutoff = 1
380 theta = 20
381 var_A = 'none' # 'iso' or 'all' or 'none'
382
383 #3: Select Location Of Vertices:
384 #vs_source controls how you get your verticies
385 #vs_source can be: 'c' to pick by clicking
386 # 'f' to read from file
387 # 't' to type below
388 vs_source = 't'
389
390 #if typing fill in here
391 #expects [x0, y0, x1, y1, wall_type*curvature sign, base index (only
matters for elongate triangle)]
392 #wall types 0 = DDW (do not use in general), 1 = elongated long side, 2 =
regular
393 #curvature sign must be 1, -1
394 #note: for elongated walls, the order of the point matters: will plot
backwards

```



```

395 typed_vs = np.array([])
396
397
398 #Can adjust what kinds of DW are plotted
399 plot_ddw = False
400 plot_iso = False
401 plot_eq1 = True
402
403 #Can turn off plotting points, lines to speed up
404 plot_points = False
405 plot_lines = True
406
407 #5: Adjust to improve fit
408 #If points need to be shifted, set True
409 #Input new values as array of [x,y], moves nearest point
410 new_points = np.array([])
411 #If curvature is backwards enter line here
412 #Input lines as array of [x0,y0,x1,y1]
413 lines_to_flip = np.array([])
414
415 #6:Rescaling
416 #Set true if you did the fitting with wrong scale and want to fix it
417 rescale = False
418 old_scale = 100
419 new_scale = scale
420
421 %%%
422 ##### CODE AREA, DO NOT TOUCH #####
423 print(Bs)
424
425 if __name__=="__main__":
426     wall_types = [plot_ddw, plot_iso, plot_eq1]
427     wall_names = ['DDW', 'Isosceles', 'Equilateral']
428
429     if vs_source == 'c':
430         n_wall = 0
431         for i in range(0, len(wall_types)):
432             if wall_types[i] == True:
433                 print('Select Wall Type {0}'.format(wall_names[i]))
434                 clicks = []
435                 img = cv2.imread(pic, 1)
436                 n_pixels = np.shape(img)[0]
437                 cv2.imshow('image', img)
438                 cv2.setMouseCallback('image', click_event)
439                 cv2.waitKey(0)
440                 cv2.destroyAllWindows()
441                 n_wall += len(clicks)/4
442                 vs_i = clicks_to_vs(clicks, i, n_wall, scale, n_pixels)
443                 if any(wall_types[0:i]) == False:
444                     vs = vs_i
445                 else:
446                     vs = np.concatenate((vs, vs_i), axis = 0)
447             elif vs_source == 'f':
448                 vs = np.loadtxt('{0}_pnts_{1}.txt'.format(pic[0:-4], suffix),
dtype=int)
449             elif vs_source == 't':
450                 vs = typed_vs
451             else:
452                 print('ERROR: MUST CHOOSE vs SOURCE')
453

```

```

454     vs = shift_points(new_points, vs, 10)
455     vs = flip_curve(lines_to_flip, vs, 5)
456     vs = match_points(vs, 5)
457
458     if rescale == True:
459         vs = rescale_vs(vs, old_scale, new_scale)
460
461     print(repr(vs))
462     plot_dw(pic, vs, A, Bs, theta, var_A, plot_points=plot_points,
plot_grid=False, suf=suffix, plot_lines=plot_lines, scale=scale, report
=True, sb=False, pix_cutoff=pix_cutoff, plot_ddw=plot_ddw)

```

8.3 Displacement field and strain calculation code

The code below is a program for extracting the interlayer displacement from STM topography maps, and calculating the strain tensor, as discussed in Chapter 4. STM topography maps are processed and imported as in Section 8.2, and their vertices are identified by the user. Vertices must be labeled with a pair of integers, representing their index in moiré supercell lattice vectors relative to an "Origin" vertex, if the lattice was unstrained. One pair of vertices, which is assumed to be unstrained, is then selected as the "model" vertex. From this the program calculates and plots the interlayer displacement and strain tensor components, interpolating from the domain wall network vertices.

Tools are built in for facilitating the accurate selection of the domain wall network vertices, as well as estimating the components of the strain tensor at an arbitrary point.

Displacement field and strain python code

```

1  """
2  Displacement Field Calculator
3  """
4
5  #####CODE AREA DO NOT TOUCH#####
6
7  import numpy as np
8  import matplotlib.pyplot as plt
9  import cv2
10 from scipy import interpolate
11 from matplotlib import ticker
12
13 #select vertices by clicking
14 def click_event(event, x, y, flags, params):
15     if event == cv2.EVENT_LBUTTONDOWN:
16         print(x, ' ', y)

```

```

17     font = cv2.FONT_HERSHEY_SIMPLEX
18     cv2.putText(img, '.', (x,y), font, 1, (255, 0, 0), 2)
19     cv2.imshow('image', img)
20     clicks.append(x)
21     clicks.append(y)
22
23 def clicks_to_vs(clicks, scale, n_pixels, pick_line=False, start=[0,0],
axis=0):
24     n_lines = int(len(clicks)/2)
25     vs_points_only = np.reshape(clicks, (n_lines, 2))
26     vs = np.zeros(shape=((n_lines, 4)), dtype=int)
27     vs[:,0:2] = vs_points_only * scale / n_pixels #switchs from default
scale to correct scale
28     vs[:,1] = -1 * vs[:,1] + scale #flips y-axis
29     if pick_line == True:
30         vs[:, axis + 2] = np.arange(start[axis], start[axis] + n_lines, 1)
31         other_axis = (axis+1)%2
32         vs[:, other_axis+2] = np.ones(n_lines) * start[other_axis]
33     return vs
34
35 #makes sure domain walls meet by matching points within a threshold radius
36 def match_points(vs, thresh):
37     matched_vs = np.copy(vs)
38     n_lines = np.shape(vs)[0]
39     for i in range(0, n_lines):
40         point1 = matched_vs[i, 0:2]
41         for j in range(i, n_lines):
42             point2 = matched_vs[j, 0:2]
43             if np.amax(abs(point1 - point2)) <= thresh:
44                 matched_vs[j, 0:2] = point1
45     return matched_vs
46
47 #shifts points within threshold radius from new point
48 def shift_points(new_points, vs, thresh):
49     matched_vs = np.copy(vs)
50     n_lines = np.shape(vs)[0]
51     for n in range(0, len(new_points)):
52         new_point = new_points[n]
53         for i in range(0, n_lines):
54             point = matched_vs[i, 0:2]
55             if np.amax(abs(new_point - point)) <= thresh:
56                 matched_vs[i, 0:2] = new_point
57     return matched_vs
58
59 #plots STM map with vertices indicated and labeled
60 def plot_points(pic, vs, suf):
61     fig, ax = plt.subplots()
62
63     ax.xaxis.set_ticks([])
64     ax.yaxis.set_ticks([])
65     ax.spines['top'].set_visible(False)
66     ax.spines['right'].set_visible(False)
67     ax.spines['bottom'].set_visible(False)
68     ax.spines['left'].set_visible(False)
69
70     #plot arrows
71     rad60 = 60 * 2*np.pi/360
72     p0 = np.array([0,0])

```

```

73     p1 = np.array([1,0])
74     p2 = np.array([0,1])
75     for i in range(0, len((vs[:,0]))):
76         if all(vs[i,2:4] == p0):
77             r0 = np.array([vs[i,0], vs[i,1], 0])
78         elif all(vs[i,2:4] == p1):
79             r1 = np.array([vs[i,0], vs[i,1], 0])
80         elif all(vs[i,2:4] == p2):
81             r2 = np.array([vs[i,0], vs[i,1], 0])
82     l1 = r1 - r0
83     rot_M = np.array([[np.cos(rad60), -1*np.sin(rad60), 0],[np.sin(rad60),
84     np.cos(rad60), 0], [0,0,1]])
85     l2 = rot_M @ l1
86     print(l1)
87     ax.arrow(r0[0], r0[1], l1[0], l1[1], length_includes_head=True, color=
88     'white', width=0.02, head_width=16, head_length=16)
89     ax.arrow(r0[0], r0[1], l2[0], l2[1], length_includes_head=True, color=
90     'white', width=0.02, head_width=16, head_length=16)
91
92     for i in range(0, len(vs[:,0])):
93         if all(vs[i,2:4] == p0):
94             ax.text(vs[i,0], vs[i,1], '0', fontsize=5, color='white')
95             ax.plot(vs[i,0], vs[i,1], marker="o", markersize=3, color='
96     white', linewidth=0)
97         else:
98             ax.text(vs[i,0], vs[i,1], '({0}, {1})'.format(vs[i,2], vs[i
99     ,3]), fontsize=5, color='white')
100             ax.plot(vs[i,0], vs[i,1], marker="o", markersize=3, color='
101     white', fillstyle='none', linewidth=0)
102
103     im = np.flip(plt.imread(pic), axis=0)
104     implot = plt.imshow(im, origin='lower', extent=[0,scale,0,scale])#,
105     extent=[500,500])
106     plt.savefig('{0}_dwf{1}.png'.format(pic[0:-4], suf), dpi=600,
107     bbox_inches='tight')
108     plt.show()
109
110     name = '{0}_{1}_pnts.txt'.format(pic[0:-4], suf)
111     np.savetxt(name, vs)
112
113
114 #shifts indices of every point so 'origin' is a t (0,0)
115 #origin = [n1, n2]
116 def shift_vs(vs, origin):
117     new_vs = np.zeros_like(vs)
118     new_vs[:,0:2] = vs[:,0:2]
119     new_vs[:,2:4] = vs[:,2:4] - origin
120     return new_vs

```

```

121 new_p0 = np.array([0,0])
122 new_p1 = np.array(p1) - np.array(p0)
123 new_p2 = np.array(p2) - np.array(p0)
124 for i in range(0, len((vs[:,0]))):
125     if all(vs[i,2:4] == new_p0):
126         r0 = np.array([vs[i,0], vs[i,1], 0])
127     elif all(vs[i,2:4] == new_p1):
128         r1 = np.array([vs[i,0], vs[i,1], 0])
129     elif all(vs[i,2:4] == new_p2):
130         r2 = np.array([vs[i,0], vs[i,1], 0])
131
132 l1 = r1 - r0
133
134 if calc_l2 == True:
135     rot_M = np.array([[np.cos(rad60), -1*np.sin(rad60), 0],[np.sin(
rad60), np.cos(rad60), 0], [0,0,1]])
136     l2 = rot_M @ l1
137 elif calc_l2 == False:
138     l2 = r2 - r0
139
140 z = np.array([0,0,1])
141 a1 = a * np.cross(z, l1) / np.linalg.norm(np.cross(z, l1))
142 a2 = a * np.cross(z, l2) / np.linalg.norm(np.cross(z, l2))
143
144 theta = a/np.linalg.norm(l1)
145 theta_z = np.array([0, 0, theta])
146
147 u = np.zeros(shape=(len(vs[:,0]), 5))
148 u_mag = np.zeros(len(vs[:,0]))
149 dis = np.zeros(shape=(len(vs[:,0]),45))
150 for i in range(0, len(vs[:,0])):
151     R = np.array([vs[i,0], vs[i,1], 0]) - r0
152     n1, n2 = vs[i,2], vs[i,3]
153     u[i,0:2] = vs[i,0:2]
154     u[i,2:5] = np.cross(theta_z, R) - n1*a1 - n2*a2
155     u_mag[i] = np.linalg.norm(u[i, 2:5]) # * 1/a #maybe this works?
156
157     dis[i,0:2] = vs[i,0:2]
158     dis[i,2:4] = vs[i,0:2] - r0[0:2] - n1*l1[0:2] - n2*l2[0:2]
159
160 #setting up displacement values
161 xs = np.linspace(0, scale, scale + 1)
162 ys = np.linspace(0, scale, scale + 1)
163 xx, yy = np.meshgrid(xs, ys)
164 points = np.rot90(np.vstack((xx.flatten(), yy.flatten()))), k=3)
165 us_list = interpolate.griddata(vs[:,0:2], u_mag, points)
166 us = us_list.reshape(len(xs),len(ys))
167 print()
168 for i in range(0,len(probe_points[:,0])):
169     print('Point: {0}'.format(probe_points[i,:]))
170     print('Displacement: {0}'.format(us[probe_points[i,0],probe_points
[i,1]]))
171     error = max(abs(us[probe_points[i,0],probe_points[i,1]] - us[
probe_points[i,0],probe_points[i,1]]),
172                 abs(us[probe_points[i,0],probe_points[i,1]] - us[
probe_points[i,0],probe_points[i,1]+err_rad]),
173                 abs(us[probe_points[i,0],probe_points[i,1]] - us[

```

```

probe_points[i,0]-err_rad,probe_points[i,1])),
174         abs(us[probe_points[i,0],probe_points[i,1]] - us[
probe_points[i,0],probe_points[i,1]-err_rad]))
175     print('Error: {0}'.format(error))
176
177     if plot_df == True:
178         rot_us = np.rot90(np.fliplr(us))
179         plot_extent = (0, scale, 0, scale)
180         plt.figure()
181         plt.contourf(rot_us, cmap='plasma', levels = 1000, extent=
plot_extent)#, locator=ticker.LogLocator())
182         plt.axis('scaled')
183         cbar = plt.colorbar(pad = 0)
184         plt.xlabel("x (nm)")
185         plt.ylabel("y (nm)")
186         cbar.set_label('', rotation=270)
187         cbar.set_ticks([0.0, 0.1, 0.2, 0.3, 0.40])
188         plt.autoscale(enable=True)
189         plt.quiver(u[:,0], u[:,1], u[:,2], u[:,3], color='black', width
=0.004, scale=2)
190         #plt.quiver(dis[:,0], dis[:,1], dis[:,2], dis[:,3], color='cyan',
width=0.004, scale=10/theta)
191         plt.savefig('df_l1_l2.png', dpi = 800)
192
193         fig, ax = plt.subplots(figsize=(6, 6))
194         ax.plot(vs[:,0], vs[:,1], marker="o", markersize=5, color='red',
fillstyle='none', linewidth=0)
195         ax.set_xlim(0, scale)
196         ax.set_ylim(0, scale)
197         for i in range(0, len(vs[:,0])):
198             ax.text(vs[i,0], vs[i,1], '{0}'.format(u_mag[i]), fontsize=8,
color='black')
199
200     return u[:,2:4]
201
202 #calculates strain tensor, plot components
203 def make_strain(vs, u, scale, probe_points, err_rad, plot=True, p0=[0.0],
p1=[1,0], p2=[0,1]):
204     #setup data sets
205     n = len(vs[:,0])
206     du = np.zeros(shape=(n, 4)) #[dux/dx, dux/dy, duy/dx, duy/dy]
207     strain = np.zeros(shape=(n, 7)) #[x_pntt, y_pnt, x_tri, y_tri, u_s,
u_H, alpha]
208     for i in range(0, n): #all point
209         coords = vs[i,2:4]
210         ind0 = np.array([i])
211         ind1 = np.where((vs[:,2:4] == coords + np.array([1,0])).all(axis
=1))[0]
212         ind2 = np.where((vs[:,2:4] == coords + np.array([0,1])).all(axis
=1))[0]
213         if ind1.size >= 1 and ind2.size >= 1:
214             ind0, ind1, ind2 = ind0[0], ind1[0], ind2[0]
215             vsi = np.stack((vs[ind0,:], vs[ind1,:], vs[ind2,:]))
216             ui = np.stack((u[ind0,:], u[ind1,:], u[ind2,:]))
217         else:
218             vsi = np.nan * np.ones(shape=(3,4))
219             ui = np.nan * np.ones(shape=(3,2))

```

```

220     l1 = vsi[1,0:2] - vsi[0,0:2]
221     l2 = vsi[2,0:2] - vsi[0,0:2]
222     Du1 = ui[1,0:2] - ui[0,0:2]
223     Du2 = ui[2,0:2] - ui[0,0:2]
224     for j in range(0,2): #axis: ux, uy
225         b = np.array([Du1[j], Du2[j]])
226         A = np.array([l1, l2])
227         x = np.linalg.solve(A, b)
228         du[i, 2*j:2*j+2] = x
229     uxx = du[i,0]
230     uyy = du[i,3]
231     uxy = 0.5*(du[i,1] + du[i,2])
232     strain_tensor = np.array([[uxx, uxy],
233                               [uxy, uyy]])
234
235     R = lambda alpha: np.array([[np.cos(alpha), -1*np.sin(alpha)],
236                                  [ np.sin(alpha),  np.cos(alpha)]]),
237     rot_ST = lambda alpha, ST: R(-1*alpha) @ ST @ R(alpha)
238
239     alpha = 0.5*np.arctan2(2*uxy, uxx - uyy)
240     uh = 0.5*(uxx + uyy)
241     us = np.sqrt((uxx - uyy)**2/4. + uxy**2)
242
243     #check everything is working right
244     rst = rot_ST(alpha, strain_tensor)
245     e0 = rst[0,0]
246     e1 = rst[1,1]
247
248     if not np.isnan(uxx):
249         assert round(rst[0,1], 10) == 0.0 and round(rst[1,0], 10) ==
0.0
250         assert round((e0 + e1)/2, 10) == round(uh, 10)
251         assert round((e0 - e1)/2, 10) == round(us, 10)
252
253     strain[i,0:2] = vsi[0,0:2] #x, y
254     strain[i,2] = (vsi[0,0] + vsi[1,0] + vsi[2,0])/3.0 #tri_x
255     strain[i,3] = (vsi[0,1] + vsi[1,1] + vsi[2,1])/3.0 #tri_y
256     strain[i,4:7] = np.array([alpha, uh, us])
257     strain = strain[~np.isnan(strain).any(axis=1)]
258
259     #plotting
260     if plot == True:
261         xs = np.linspace(0, scale, scale + 1)
262         ys = np.linspace(0, scale, scale + 1)
263         xx, yy = np.meshgrid(xs, ys)
264         points = np.rot90(np.vstack((xx.flatten(), yy.flatten()))), k=3)
265
266     #heterostrain plot
267     us_list = interpolate.griddata(strain[:,2:4], strain[:,5], points)
268     us = us_list.reshape(len(xs), len(ys))
269     print()
270     for i in range(0, len(probe_points[:,0])):
271         print('Point: {0}'.format(probe_points[i,:]))
272         print('Heterostrain: {0}'.format(us[probe_points[i,0],
probe_points[i,1]]))
273         error = max(abs(us[probe_points[i,0], probe_points[i,1]] - us[
probe_points[i,0]+err_rad, probe_points[i,1]]),

```

```

274         abs(us[probe_points[i,0],probe_points[i,1]] - us[
probe_points[i,0],probe_points[i,1]+err_rad])),
275         abs(us[probe_points[i,0],probe_points[i,1]] - us[
probe_points[i,0]-err_rad,probe_points[i,1]])),
276         abs(us[probe_points[i,0],probe_points[i,1]] - us[
probe_points[i,0],probe_points[i,1]-err_rad]))
277     print('Error: {0}'.format(error))
278     rot_us = np.rot90(np.fliplr(us))
279     plot_extent = (0, scale, 0, scale)
280     plt.figure()
281     plt.contourf(rot_us, cmap='coolwarm', levels = 1000, extent=
plot_extent)#, vmin=-0.0012, vmax=0.0032)#, locator=ticker.LogLocator()
)

282     plt.axis('scaled')
283     cbar = plt.colorbar(pad = 0)
284     plt.xlabel("x (nm)")
285     plt.ylabel("y (nm)")
286     cbar.set_label('', rotation=270)
287     cbar.set_ticks([-0.0012, -0.001, -0.0008, -0.0006, -0.0004,
-0.0002, 0.0, 0.0002, 0.0004, 0.0006, 0.0008, 0.001, 0.0012])
288     # cbar.set_ylim(-0.0006, 0.0012)
289     plt.autoscale(enable=True)
290     plt.savefig('uh.png', dpi = 800)
291
292     #shear strain plot
293     us_list = interpolate.griddata(strain[:,2:4], strain[:,6], points)
294     us = us_list.reshape(len(xs),len(ys))
295     print()
296     for i in range(0,len(probe_points[:,0])):
297         print('Point: {0}'.format(probe_points[i,:]))
298         print('Shear Strain: {0}'.format(us[probe_points[i,0],
probe_points[i,1]]))
299         error = max(abs(us[probe_points[i,0],probe_points[i,1]] - us[
probe_points[i,0]+err_rad,probe_points[i,1]]),
300         abs(us[probe_points[i,0],probe_points[i,1]] - us[
probe_points[i,0],probe_points[i,1]+err_rad])),
301         abs(us[probe_points[i,0],probe_points[i,1]] - us[
probe_points[i,0]-err_rad,probe_points[i,1]])),
302         abs(us[probe_points[i,0],probe_points[i,1]] - us[
probe_points[i,0],probe_points[i,1]-err_rad]))
303         print('Error: {0}'.format(error))
304         rot_us = np.rot90(np.fliplr(us))
305         plot_extent = (0, scale, 0, scale)
306         plt.figure()
307         plt.contourf(rot_us, cmap='Purples', levels = 1000, extent=
plot_extent, vmin=-0.0025)#, vmax=0.0025)#, locator=ticker.LogLocator()
)

308     plt.axis('scaled')
309     cbar = plt.colorbar(pad = 0)
310     plt.xlabel("x (nm)")
311     plt.ylabel("y (nm)")
312     cbar.set_label('', rotation=270)
313     cbar.set_ticks([0.0, 0.0005, 0.0010, 0.0015, 0.0020, 0.0025,
0.003, 0.0035, 0.004, 0.0045, 0.005])
314     #cbar.set_ylim(0.0, 0.0025)
315     plt.autoscale(enable=True)

```



```

316     plt.savefig('us.png', dpi = 800)
317
318     #angle plot
319     us_list = interpolate.griddata(strain[:,2:4], strain[:,4], points)
320     us = us_list.reshape(len(xs),len(ys))
321     rot_us = np.rot90(np.fliplr(us))
322     plot_extent = (0, scale, 0, scale)
323     plt.figure()
324     plt.contourf(rot_us, cmap='cividis', levels = 1000, extent=
plot_extent, vmin=-1*np.pi/2, vmax=np.pi/2)#, locator=ticker.LogLocator
    ())
325     plt.axis('scaled')
326     cbar = plt.colorbar(pad = 0)
327     plt.xlabel("x (nm)")
328     plt.ylabel("y (nm)")
329     cbar.set_label('', rotation=270)
330     cbar.set_ticks([-3*np.pi/4, -1*np.pi/2, -1*np.pi/4, 0., np.pi/4,
np.pi/2 ])
331     cbar.set_ticklabels(['-3pi/4', '-pi/2', '-pi/4', '0', '-pi/4', '-pi/2
',])
332     # cbar.set_ylim(-1*np.pi/2, np.pi/2)
333     plt.autoscale(enable=True)
334     plt.savefig('alpha.png', dpi = 800)
335
336     return du, strain
337
338 #can use to scale you vs list if you had the wrong scan size initially
339 def descale_vs(vs,x_scale,y_scale):
340     #print(vs)
341     descaled_vs = np.zeros_like(vs)
342     descaled_vs[:,0] = vs[:,0]/x_scale
343     descaled_vs[:,1] = vs[:,1]/y_scale
344     descaled_vs[:,2:4] = vs[:,2:4]
345     #print(descaled_vs)
346     return descaled_vs
347
348 def flip_vs(vs,scale,flip_x=False,flip_y=False):
349     flip_vs = np.copy(vs)
350     if flip_x == True:
351         flip_vs[:,0] = -1*(flip_vs[:,0] - scale/2.0) + scale/2.0
352     if flip_y == True:
353         flip_vs[:,1] = -1*(flip_vs[:,1] - scale/2.0) + scale/2.0
354     return flip_vs
355
356 #####INPUTS HERE#####
357
358 #1: Import STM Map
359 #pic is path to scan file
360 #suffix is appended to scan file name when saving
361 pic = ''
362 suffix = 'df'
363 scale = 500 #Scan size in nm
364
365
366 #2: Select Location Of Vertices:
367 #vs_source controls how you get your vertices
368 #vs_source can be: 'c' to pick by clicking
369 #                  'f' to read from file
370 #                  't' to type below

```

```

371 vs_source = 't'
372
373 #if typing fill in here
374 #expects [x, y, n1, n2]
375 #x and y are vertex location in nm, n1 and n1 are indices
376 #n1 and n2 generally must be filled in by hand
377 typed_vs = np.array([])
378
379 #auto populates n1, n2 based on index of first point clicked ('start')
380 #gnerally doesn't work in practice but can speed things up
381 pick_line = True
382 start = [0,0] #[n1,n2]
383 axis = 0
384
385 #Can correct points here without finding them in vs
386 #If points need to be shifted, input new values as array of [x,y]
387 new_points = np.array([])
388
389
390 #3: Identify Unstrained Region
391 #The triangle with vertices with indices p0,p1,p2 is assumed to be
    unstrained
392 #Will perform displacement calculation assuming unstrained moire UC
    vectors are l1=p1-p0, l2=p2-p0
393 p0 = [0,0]
394 p1 = [1,0]
395 p2 = [0,1]
396 calc_l2 = True #will assume second lattice vector in just p1-p0 rotated 60
    deg
397
398 #3: Probe points
399 #select point for extracting strain values based on interpolation
400 #expects [x, y,]
401 #err_rad is radius in nm used to calculate uncertainty
402 probe_points = np.array([])
403 err_rad = 5 #nm
404
405 #4: Plot
406 plot_vs = True
407 plot_df = True
408 plot_strain = True
409
410
411 if __name__=="__main__":
412
413     if vs_source == 'c':
414         n_click = 0
415         clicks = []
416         img = cv2.imread(pic, 1)
417         n_pixels = np.shape(img)[0]
418         cv2.imshow('image', img)
419         cv2.setMouseCallback('image', click_event)
420         cv2.waitKey(0)
421         cv2.destroyAllWindows()
422         n_click += len(clicks)/2
423         vs = clicks_to_vs(clicks, scale, n_pixels, pick_line=pick_line,
            start=start, axis=axis)
424     elif vs_source == 'f':
425         vs = np.loadtxt('{0}_{1}_pnts.txt'.format(pic[0:-4], suffix, dtype
            =int))

```

```
426     elif vs_source == 't':
427         vs = typed_vs
428     else:
429         print('ERROR: MUST CHOOSE vs SOURCE')
430
431     #5: Options for correcting
432     #for moving points
433     #vs = shift_points(new_points, vs, 0)
434     #vs = match_points(vs, 0)
435
436     #For streching all the point in x and y
437     #vs = descale_vs(vs,400.0/289,400.0/289)
438
439
440     #####CODE AREA DO NOT TOUCH#####
441     vs = vs.astype(int)
442     vs = shift_vs(vs, [0,0])
443     print(repr(vs))
444     if plot_vs == True:
445         plot_points(pic, vs, suffix)
446
447     u = make_displacment(vs, scale, probe_points, err_rad, calc_l2=calc_l2
448     , plot_df = plot_df, p0=p0, p1=p1, p2=p2)
449     du, strain = make_strain(vs, u, scale, probe_points, err_rad, plot=
450     plot_strain, p0=p0, p1=p1, p2=p2)
```

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