MBE GROWTH AND STM STUDY OF CHALCOGENIDE THIN FILMS

BY

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DISSERTATION

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics in the Graduate College of the University of Illinois at Urbana-Champaign, 2021

Urbana, Illinois

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Abstract

This dissertation focuses on the physics of ultra-thin films with properties influenced by their interface with the underlying substrate. Thin films have many interesting properties, of which the main one motivating the work here has been superconductivity. Studying 2D and quasi-2D systems is key to our understanding of high $T_c$ superconductivity. But although the motivation of this dissertation has been the study of superconductivity, the actual phenomena studied in this dissertation have been film-substrate interactions, through strain, through phonons, through charge transfer, through Moiré patterns.

In the first main chapter, we explore the growth of a monolayer of tin diselenide on highly oriented graphite. It exhibits a gap in the density of states, and we walk through the process of testing whether this is a superconducting gap. We show that monolayer tin diselenide is not a superconductor, and that instead we have to seek another explanation to explain its electronic structure, which leads us to considering the Moiré patterns it forms as periodic perturbations to the Hamiltonian, or electron-phonon interactions.

Next, we grew FeSe on SrTiO$_3$ (001). The growth process was improved, although we did not grow the superconducting monolayer. Energy-dependent density of states was measured as a function of film thickness, showing the change in band structure with thickness, including the bands intersecting the Fermi energy. For greater film thickness, emergence of different nematic / structural domains was observed, and the differences in electronic states were measured via quasiparticle interference.

We grew thin films of the alloy Fe(Se$_x$Te$_{1-x}$) on SrTiO$_3$ (001) for values of $x$ ranging from 0.19 to 0.79. Comparison of tunneling spectra across compositions show qualitative agreement with band structure predictions. Nanoscale strain was measured on the surface of the samples and spectra are compared in differently strained regions, albeit with ambiguous results rather than support for strain as the driver for the band structure changes as a function of thickness. Some evidence of topological modes at screw dislocations is also presented.
To Jocelyn for giving me tours.
Acknowledgments

This venture would not have been possible without a huge support network surround it. I would like to thank my parents, brothers, and sisters for their support both emotional and comestible. I would like to thank the University of Illinois in general and the Physics department and Materials Research Laboratory in specific for providing both equipment and expertise. More generally, this would not have been possible without financial support for physics from the National Science Foundation (award 1629068), the Department of Energy (award DE-SC0014335f), and the Gordon and Betty Moore Foundation (grant GBMF4860). I would like to thank all of my labmates over the years, especially Hamood Arham, Daniel Walkup, Kane Scipioni, Zhenyu Wang, Yulia Maximenko, Davide Iaia, Guannan Chen, Jorge Olivares, Leena Aggarwal, Lin Jiao, and Arjun Ragavan. And thanks to Lance Cooper, Wendy Wimmer, all my teachers, and especially my advisor Vidya Madhavan for putting up with me.
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<tbody>
<tr>
<td>2DEG</td>
<td>Two-Dimensional Electron Gas</td>
</tr>
<tr>
<td>ARPES</td>
<td>Angle-Resolved Photoemission Spectroscopy</td>
</tr>
<tr>
<td>BCS</td>
<td>Bardeen-Cooper-Schrieffer</td>
</tr>
<tr>
<td>BZ</td>
<td>Brillouin Zone</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of States</td>
</tr>
<tr>
<td>LDOS</td>
<td>Local Density of States</td>
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<tr>
<td>MBE</td>
<td>Molecular Beam Epitaxy</td>
</tr>
<tr>
<td>PID</td>
<td>Proportional-Integral-Derivative</td>
</tr>
<tr>
<td>QCM</td>
<td>Quartz Crystal Microbalance</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford Backscattering Spectrometry</td>
</tr>
<tr>
<td>RHEED</td>
<td>Reflected High-Energy Electron Diffraction</td>
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<tr>
<td>SOC</td>
<td>Spin-Orbit Coupling</td>
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<tr>
<td>SP-STM</td>
<td>Spin-Polarized Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
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<tr>
<td>STO</td>
<td>Strontium Titanate (SrTiO₃)</td>
</tr>
<tr>
<td>STS</td>
<td>Scanning Tunneling Spectroscopy</td>
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<tr>
<td>UHV</td>
<td>Ultra-High Vacuum</td>
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Chapter 1

Introduction

1.1 Summary

This dissertation reports on the subset of experiments I’ve been involved in where I both grew the samples and did the scanning tunneling microscopy (STM). These have focused on very thin crystalline films, because of the unique capabilities of STM to study the surfaces of such films, and the specialization of the molecular beam epitaxy (MBE) vacuum chamber that I designed and used.

In the introduction we’ll touch on some general topics in condensed matter physics useful for putting later chapters in context. Specific background on the study of specific materials will be relegated to the introductions of their specific chapters.

Because thin films and layered materials were studied, we start with the basics of electronic states in two-dimensional materials. To understand the effects we might see, we need to complicate the basic picture by also considering electron-phonon coupling and spin-orbit coupling. Some context on superconductivity and topological phases is also necessary.

1.2 Two-dimensional Electronic States

Layered materials such as SnSe$_2$ or FeSe have covalent bonding between two-dimensional sheets of atoms, but only Van-der-Waals bonding in between neighboring sheets. This causes them to be quasi-two-dimensional (quasi-2D) both structurally and electronically. Structurally, this means that growing these crystals on a flat surface will result in growing large flat sheets, and that if you grow a large single crystal of one of these materials and break it, the cleavage planes will lie between the layers, both of which are very useful properties for experimental surface probes. Electronically, it means that conductivity is larger in-plane and smaller out of plane and that the electron density of states (DOS) and interactions depend strongly on the in-plane component of the wavevector but only weakly on the out of plane component. See Fig. 1.1 for a comparison of 3D vs. quasi-2D Fermi surfaces. We might expect 2D and quasi-2D systems to have qualitatively different
electronic properties from 3D systems because of considerations such as the Mermin-Wagner theorem which suggests 2D systems have difficulty breaking continuous symmetries (though there are still possibilities like the Kosterlitz-Thouless transition [1]) but more ways to form domain walls. Lowered dimensionality also factors into screening [2] and localization [3] in ways that can increase electron-electron interactions.

Figure 1.1: a: Fermi surface of Cu Fermi surface, from Segall 1962 [4]. Polyhedron is the Brillouin zone. Almost totally isotropic in all three dimensions. b and c: Perspective view and top view of FeSe Fermi surface, from Subedi et al. 2008 [5]. Rectangular prism is the Brillouin zone. There’s only slight dependence on the z component of the wavevector, and the 2D view of the Fermi surface maintains most information about it.

Therefore when we start with a basic single-particle Hamiltonian

\[ H = \frac{p^2}{2m} + V(r) \]  

(1.1)

or a basic quasiparticle Hamiltonian

\[ H = (\epsilon_k - \mu)c_k^\dagger c_k \]  

(1.2)

we can mostly think of the solutions in terms of periodic Bloch states that live in the 2D plane.

Because they’re so common, it’s important to introduce the anatomy of the two most common reciprocal lattices in 2D. A triangular real-space lattice gives rise to a (rotated) triangular reciprocal lattice, and likewise a square real-space lattice gives rise to a square reciprocal lattice. The high symmetry points in reciprocal space have conventional labels. For a triangular lattice with hexagonal Brillouin zone (BZ), the center is \(\Gamma\), the corner of the Brillouin zone is \(K\), and the center of the Brillouin zone edge is \(M\). For the square lattice it’s the corner that’s conventionally labeled \(M\) and the center of the edge is labeled \(X\).
1.2.1 Spin-orbit Coupling

Spin-orbit coupling refers to the change in energy of an electron in a magnetic field, $\Delta V = -\mu \cdot B$. $\mu$ is the intrinsic magnetic moment of the electron, given by

$$\mu = g \frac{e \hbar}{4m} \sigma \quad (1.3)$$

where $i$ and $m$ are the charge and mass of the electron, $\sigma$ are the unit Pauli matrices, and $g$ is the gyromagnetic ratio which for (free) electrons is approximately 2.

For electrons orbiting an atom, which we can simplify by thinking about the hydrogen-like atomic potential for element number $Z$: $V(r) = -Ze/r$ with magnetic field (in the reference frame of the electron) $B = v \times E$. In this model the lowest-order correction is of order $\Delta E \approx Z^4 \alpha^2 \cdot 13.6\text{eV} [6]$, where $\alpha$ is the fine structure constant (approx. $1/137$). In short, the heavier the atom, and the closer the electron is to the nucleus, the higher the velocity ($p/m$) and the magnetic field, and the larger the shift.

For crystalline materials, the electrons live in periodic states with a certain orbital character rather than orbitals around individual atoms, where “orbital character” can be quantified as the (norm squared) overlap between the extended energy eigenstate and particular orbitals of a standalone atomic potential. The energy shift due to spin-orbit coupling of these states depends, as above, on the electron density and velocity distribution, particular near the atomic nuclei. This distribution can depend on the orbital angular
momentum of the electron, shifting the energy of bands relative to each other even if they may have been degenerate otherwise [7]. This energy shift can be on the scale of tens of meV (e.g. Surh et al. 1991 calculating the band structure of GaAs [8]).

1.3 Electron-Phonon Coupling

Vibrations of the atomic nuclei in a crystal have a dispersion relation just as the electrons do. These vibrations are quantized, and individual excitations can propagate as quasiparticles, called phonons. Analogous to photons, phonons have momentum of $\hbar k$, although because of the periodicity of the lattice this is really a ’crystal momentum’ defined only modulo $2\pi/a$ (or more generally, translation by the reciprocal lattice vectors), and energy $\hbar \omega$. Compared to electrons, phonons typically have much lower energies for a given momentum, which we might rephrase as saying that the stiffness of the atomic lattice is smaller than the “stiffness” of the electron wavefunction for most values of wavevector $k$. Exactly as with simple harmonic oscillators, higher masses vibrate more slowly, and so phonons in crystals with lighter elements (e.g. carbon, oxygen) tend to have higher $\omega$ and thus higher energy than in crystals with heavier elements.

Electrons can interact with phonons via the electric field. We can think of this as lattice distortions creating a periodic potential with wavevector $q$, which then allows for interactions between electron states.

![Figure 1.3: a: Phonon spectrum of graphite, from Young 1965 [9]. b: Partial phonon spectra of FeSe on SrTiO$_3$, from Li et al. 2014 [10]. Note how the highest energy phonons are attributed to vibration of oxygen atoms.](image)
connected by the scattering vector $\mathbf{q}$ and offset by the phonon energy $\hbar \omega$. This interaction renormalizes
the dispersion relation, but only near the Fermi energy because scattering requires occupied and unoccupied
states within $\hbar \omega$. For the simplest case, this reduces the group velocity (flattening the band) at the Fermi
energy by

$$v(k) = \frac{1}{\hbar} \frac{\partial \epsilon(k)}{\partial k} = \frac{1}{1 + \lambda_k} v_0(k)$$  \hspace{1cm} (1.4)$$

where this parameter $\lambda_k$, called the mass enhancement factor because the effective mass is given by
$m_{\text{eff}} = (1 + \lambda_k)m_0$, is the integral of the amount of electron-phonon interaction:

$$\lambda_k = 2 \int d\omega \frac{\alpha^2(\omega)F_k(\epsilon_k, \omega)}{\omega}.$$  \hspace{1cm} (1.5)$$

This term, $\alpha^2(\omega)F_k(\epsilon_k, \omega)$, often simplified to $\alpha^2 F(\omega)$, is a common enough that it has a particular name,
the Eliashberg function, after Gerasim Eliashberg, who gave an account of electron-phonon interactions in
the context of superconductivity [11]. Taken as a whole it can be thought of as the probability density of
phonon emission or absorption, where $\alpha^2$ is the electron-phonon coupling term and $F(\omega)$ is the density of
phonon states.

The corrections to the electron self-energy $\Sigma$ due to electron-phonon coupling can also be given in terms
of the Eliashberg function, split into imaginary and real parts, with $f$ being the Fermi-Dirac distribution
and $b$ being the Bose-Einstein distribution.

$$\text{Im}(\Sigma) = \pi \int_0^\infty d\omega(\alpha^2 F_k(\epsilon, \omega)(2b(\omega) + f(\omega + \epsilon) + f(\omega - \epsilon)))$$  \hspace{1cm} (1.6)$$

$$\text{Re}(\Sigma) = \frac{1}{\pi} \int d\epsilon \frac{\text{Im}(\Sigma(\epsilon'))}{\epsilon - \epsilon'}$$  \hspace{1cm} (1.7)$$

The imaginary part represents the quasiparticle lifetime (or rather, the decrease in it due to the electron-
phonon interaction), and can be measured relatively directly by techniques such as angle-resolved photo-
mission spectroscopy that can measure the linewidth of the electron density of states [14][15]. The real
part can be measured via spectroscopy as the displacement between the actual renormalized dispersion rela-
tion and the phonon-free dispersion relation inferred from higher energy scales (as in [16]). The Eliashberg
function is often approximated as being proportional to the second derivative of the tunneling conductance,
$\frac{d^2 I}{dV^2}$. Given their mathematical relationship above (or even just using the general Kramers-Kronig relations),
direct measurement of one can be used to infer the other.
1.4 Superconductivity

1.4.1 BCS

Although superconductivity is a ubiquitous topic, I will nonetheless give some short details covering what is used later.

Conventional superconductors, such as metals like Al or Pb that are cooled below their superconducting transition temperature, operate by the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity [17]. In BCS theory, an attraction is postulated between electrons as a two-electron term in the Hamiltonian

$$H_1 = \sum_{\mathbf{k}, \mathbf{k}'} -V(\mathbf{k}, \mathbf{k}')$$

where $V(\mathbf{k}, \mathbf{k}')$ is just some positive constant for those $\mathbf{k}, \mathbf{k}'$ whose energy is close to the Fermi surface (within some distance $\hbar \omega$, and zero elsewhere. Migdal [18] and Eliashberg [11] showed precisely how this net attractive potential between electrons could be explained by electron-phonon interactions. This naturally
leads to an electronic ground state with an energy gap that can nonetheless carry current when an electric field is applied.

Superconductors exhibit the Meissner effect[19], expelling magnetic fields below the transition temperature. The necessary current flows are described by the (originally purely phenomenological) London equation

\[ J = -\frac{n_s e^2}{mc} A \]  

where \( J \) is the current, \( n_s \) is the density of superconducting electrons, \( e \) is the unit of charge, \( m \) is the mass of the electron, and \( A \) is the magnetic vector potential in the Coulomb gauge \( \nabla \cdot A = 0 \) [20]. This rule leads magnetic fields inside a superconductor to decay exponentially with penetration depth, also called the London penetration depth,

\[ \lambda = \frac{m}{\mu_0 n_s e^2} \]  

\( \mu_0 \) being the vacuum permeability. The penetration depth is in a sense the inverse of how easily current can be moved inside the superconductor.

In addition to the penetration depth, another important quantity characterizing a superconductor is the superconducting coherence length,

\[ \xi_0 = \sqrt{\frac{\hbar^2}{4ma}} \]  

, where \( \alpha \) is a phenomenological parameter from Ginzburg-Laundau theory that behaves like \( \alpha = \alpha_0(T_c - T) \) near the superconducting transition [21]. In a BCS superconductor, we can approximate the coherence length by

\[ \xi_{BCS} = \frac{\hbar v_F}{\pi \Delta} \]  

where \( v_F \) is the Fermi velocity and \( \Delta \) is the size of the superconducting energy gap. The superconducting coherence length defines how difficult it is for \( n_s \) to vary in space. Competition between the penetration depth and the coherence length determines whether, under strong magnetic field, the superconducting state will be destroyed all at once or whether it will allow magnetic vortices to penetrate through the bulk first. If \( \lambda/\xi > 1/\sqrt{2} \) it forms vortices (is a type-II superconductor) while if \( \lambda/\xi < 1/\sqrt{2} \) the superconductivity is destroyed all at once (type-I). Many pure metals exhibit type-I superconductivity, but few other materials.

1.4.2 Non-BCS

Superconductors that don’t follow BCS superconductivity date back to at least 1979, with the measurement of heavy-fermion material CeCu$_2$Si$_2$ by Steglich [22]. Unlike in BCS where the Hamiltonian and resulting su-
perconducting state are isotropic, nuclear magnetic resonance relaxation rate and specific heat measurements showed power-law rather than exponential dependence on temperature, indicating nodes in the gap, which has been interpreted as a fourfold “d-wave” symmetry rather than isotropic “s-wave” symmetry. Then in 1986, there was the discovery of high-temperature superconductivity in LaBaCuO$_4$ by Bednorz and Müller [23], with $T_c$ of 35 °K (significantly higher than runner-ups like Nb$_3$Sn[24] already pushing the limits of the electron-phonon pairing mechanism) with similarly non-BCS gap symmetry[25]. A complete survey of unconventional superconductors is impossible, but includes further cuprates, heavy fermions[26][27], organic superconductors[28], and relatively recent discoveries in iron-based superconductors[29].

These non-BCS superconductors have many commonalities but no universals. Two such non-universal patterns that are relevant to this dissertation are quasi-2D dimensionality (among cuprates, iron-based superconductors, and some heavy fermion materials) and low density of states at the Fermi level (with rare exceptions). Normal BCS superconductors have enhanced $T_c$ when the DOS at the Fermi level is high, possibly because $T_c$ is being set relative to the Fermi temperature scale $T_F$, or because a peak in DOS increases the Fermi velocity, increasing the BCS coherence length and decreasing the width of the thermal momentum distribution of electrons [30]. But unconventional superconductors tend to break this rule and can have high $T_c$ with low DOS.

### 1.5 Topological Phases

Different phases of matter are typically distinguished from each other by qualitatively different values of some order parameter. In water, for example, we might distinguish the solid and liquid phases based on the degree of long-range correlation in atomic positions. Topological phases of matter are so-called because the order parameter is a topological invariant. Not in the sense that the system has some unusual shape, but in the sense that there are properties of the band structure that are preserved under continuous deformation of it, which can take different values in different materials.

What we would now call topological order was first studied as the quantum Hall effect. When a 2D gas of electrons is placed in an external magnetic field, the allowed energy levels of the electrons are quantized into what are called Landau levels. When Hall effect measurements are made of this system, the Hall conductance is quantized in units of $e^2/h$ [31], even in a system with disorder and thermal broadening of the distribution. This was explained by reference to the boundary conditions imposed on individual Landau level states [32]. However, in a periodic potential such as a real crystal lattice, Landau levels split into a large number of sub-bands, each of which could potentially contribute its own quantum of conductance. This was resolved
by Thouless, Kohmoto, Nightengale, and den Nijs, who calculated the Hall conductance and found that the
collection from each sub-band was given by either a positive or negative integer multiple of $e^2/h$ [33].
These integers are topological invariants of the sub-bands, called Chern numbers [34].

To understand modern interest in topological insulators, however, we should move on from the quantum
Hall effect to the spin Hall effect and quantum spin Hall effect. The spin Hall effect, specifically the intrinsic
spin Hall effect, is the accumulation of spin-polarized electrons on the edges of a wire carrying a current.
Unlike the general Hall effect, this effect only appears in special materials. It was predicted for GaAs [35][36]
because the valence band is split into branches due to spin-orbit coupling, and the states in these branches
are not eigenstates of angular momentum along the direction of travel. Current flow ends up generating a
spin current

$$J^i_j = \sigma_{SH} \epsilon^{ijk} E_k$$

(1.13)

where $\sigma_{SH}$ is the spin Hall conductivity, $\epsilon^{ijk}$ is the antisymmetric tensor, $E_k$ the applied electric field in
the k direction, $j$ is the direction of spin current flow, and $i$ is the spin component. So if a field is applied
along the z-direction, spin current of $+x$ spins will flow in the y-direction. In an important sense this is all
because of helicity in the band structure, due to a breaking of inversion symmetry and coupling between
spin and momentum. Correlation between spin and momentum in the valence bands leads to the spin Hall
effect when the split bands have different density of states. After the prediction, the spin Hall effect was
quickly observed in the lab [37][38].

The quantum spin Hall effect refers to the quantization of the spin Hall conductance in units of $e/2\pi$. In
2005 Kane and Mele suggested that graphene with sufficient spin-orbit coupling would exhibit the quantum
spin Hall effect [39]. Then, in 2006, Berenvig and Zhang predicted that a quantum spin Hall surface state
could be found in quantum wells of HgTe [40], and the predicted effect was observed in 2007 [41]. Around
this same time, the realization was made, primarily by Fu, Kane, and Mele, that the quantum spin Hall
state was topologically distinct from the ordinary state [42]. In quantum Hall systems the topological order
parameter was expressed as an integral enclosing part of the Brillouin zone [33], but generalizing this to 3D
required characterizing the band structure by four $Z_2$ indices [43][44], which can be calculated by an integral
over the occupied electronic states, or also often by properties like parity of the band structure at certain
high-symmetry points in reciprocal space.

Topological insulators, finally, are materials that have quantum spin Hall states on their surface inside
a gap in the bulk bands, guaranteed by a topological property of the band structure. This nontrivial band
structure can be thought of as arising from band “inversion,” where spin-orbit coupling corrections can change
the orbital character associated with different bands. This has been studied by tuning the composition of a
doped crystal across the topological phase transition [45][46]. Because this is a discontinuous process, the bands involved must close their gap and become degenerate at at least one point during the transition.

This fact also explains the relationship between topology and surface states; because the vacuum is topologically trivial, crossing from a topological insulator to the vacuum requires closing the gap at the surface to undo the band inversion. This gapless surface state has correlated spin and momentum, also called spin-momentum locking, which is responsible for the spin Hall effect. Because scattering a surface state electron now also requires flipping its spin, most scattering processes are suppressed and the surface state is practically non-dissipative.

Topological phases are a field where theory tends to be ahead of experiment. The topological insulators Bi$_x$Sb$_{1-x}$ was predicted in [43] and later confirmed by ARPES measurements [47]. The same is true for topological insulator Bi$_3$Se$_3$ [48][49] and topological crystalline insulator SnTe [50][51].

### 1.6 Appendix: Density Functional Theory

Calculated band structures and electronic states are cited commonly in later chapters. These are mostly calculated using density functional theory (DFT). The namesake density functional comes from the Hohenberg-Kohn theorems that the energy of an electronic system is completely determined by the density (i.e. is a density functional), and that the density is uniquely determined by the potential [52]. Unfortunately these theorems are non-constructive, but later Kohn and Sham would provide a decomposition of the energy functional into terms that allow for calculation in terms of non-interacting electrons plus some Hartree-Fock style correction term [53]. This was a breakthrough because it reduces the dimensionality of the problem of predicting the density by numerical minimization of the energy. The general breakdown of the functional is

$$F[\rho] = \text{Orbital KE} + \text{Coulomb} + \text{Exchange}$$

(1.14)

where the orbital term is due to the kinetic energy of the non-interacting orbital functions used as starting points (similar to Wannier states) in the Kohn-Sham method, the Coulomb term is due to electron-electron repulsion proportional to $1/2 \int \int dx dy \rho(x) \rho(y)/|x - y|$, and the exchange term is essentially a blanket term covering necessary corrections to the energy. The exact form of this correction term is one of the free parameters in a DFT calculation, and is usually denoted by one of the acronyms such as LDA (local density approximation, originally from Kohn and Sham [53]), PBE (after Perdew, Burke, and Enzerhof [54]), or B3LYP (after Becke, Lee, Yang and Parr [55] [56]).

DFT is very useful for calculating the approximate band structure, but is notoriously inaccurate about
the exact sizes of bandgaps [57]. Methods can be used to correct the gap sizes in a DFT calculation, but
this is often a post-hoc choice made in light of some knowledge about the material in question. Thus
when our measurements later disagree with calculated gap sizes, this will not be remarked upon. Another
problem for DFT is calculation of weak interactions such as induced-dipole-induced-dipole interactions that
are important for holding together the layered materials studied in later chapters. In general we don’t expect
the DFT band structure to account for low-energy corrections. Despite these issues, DFT predictions are
still extremely useful to compare to.
Chapter 2

Scanning Tunneling Microscopy

In this chapter we discuss scanning tunneling microscopy (STM)[58][59]: its overall properties, the basic physical principles behind its operation, and the specifics of several applications we take advantage of in this thesis. In particular, we need to give in-depth explanations of scanning tunneling spectroscopy, quasiparticle interference, and the Lawler-Fujita drift correction procedure that we can use to measure nanoscale strain.

2.1 Basics of Scanning Tunneling Microscopy

Scanning tunneling microscopy is a member of the family of scanning probe microscopy techniques, where a sharp tip is scanned over the surface and senses the properties of the surface as it travels. In STM, the surface is sensed by the quantum-mechanical tunneling current between the tip and sample. We apply a bias voltage between the two (in our case, biasing the sample while the tip is held at the ground voltage of the electronics), on the order of 1 mV to 1 V, and then measure current on the order of $10^{-12}$ A (1 pA) to $10^{-9}$ A (1 nA). The tip is positioned in X, Y, and Z by piezoelectric actuators with sub-Ångstrom precision. Normally, the tip is held at a fixed height (typically around 0.5 nm [60]) relative to the surface by a PID feedback loop that moves the tip away ("up") when the tunneling current is above a set point, and towards ("down") when the tunneling current is too low. With the feedback loop on, the tip can be scanned over the surface in the X and Y directions, and the height recorded, to give a topographic image of the surface.

The typical way to understand the tunneling current is in terms of Bardeen’s tunneling formula [61][62]. If we assume that the sample and tip states are almost orthogonal and the rate of tunneling is small, Fermi’s golden rule tells us that the tunneling current is:

$$I \approx \frac{2\pi e}{h} \sum_{n_t,n_s} \delta(E_t - E_s - \Delta\mu)(F_t(E_t)(1 - F_s(E_s)) - (1 - F_t(E_t))F_s(E_s))|M_{ts}|^2$$

(2.1)

Where $F_t$ is the Fermi-Dirac distribution of the tip, given its temperature and chemical potential, and likewise for $F_s$ and the sample. Tunneling is assumed to only occur between states of the same energy, which in terms of the indexing of tip and sample states can be thought of as having single-particle energies offset
by the difference in chemical potential $\Delta \mu$. The rate of tunneling between two states is governed by a matrix element $M_{ts}$, which depends on the overlap between the tip and sample states.

For STM, the tunneling matrix elements are approximated by the Tersoff-Hamann formula \cite{63}, which assumes that tip is spherically symmetric:

$$|M(\psi_{t,j}, \psi_{s,n})|^2 \approx \frac{\hbar^4}{m^2} |A_j|^2 |\psi_{s,n}(0)|^2$$  

(2.2)

Where $A_j$ is the amplitude of the long-range exponential approximation to the tip state, and $\psi_{s,n}(0)$ is the amplitude of the sample state at the center of curvature of the tip. This is important for STM, because it means that a round tip is genuinely measuring the sample wavefunction at a single point, albeit a point farther above the surface than the actual edge of the tip. Chen, however, points out that for realistic scanning distances this model can’t account for the observed atomic corrugations on certain metals, and proposed modeling the tip with a terminal atom with a dangling d orbital\cite{64}. If the tip wavefunction is not s-wave, the current can reflect spatial derivatives of the sample wavefunction at the tip: e.g. the derivative in the

---

Figure 2.1: Diagram showing the sample surface and STM tip, the piezoelectric actuators, and the electronic feedback loop.
x direction for the \(d_{xz}\) orbital. For practical purposes, however, we select tips where these spurious signals are small.

If we approximate these sums over states by integrals over energy, we get a formula in terms of the density of states of the tip and sample, implicitly allowing us to infer the approximate density of states from the tunneling current.

\[
I \propto \int_{E_t, E_s} \delta(E_t - E_s - \Delta \mu) \cdot \left( (F_t(E_t)(1 - F_s(E_s)) - (1 - F_t(E_t))F_s(E_s)) \right) \cdot DOS_t(E_t) DOS_s(E_s) |M(E_t, E_s)|^2 \, dE_t \, dE_s
\]  \hspace{1cm} (2.3)

In ideal conditions we can further assume that the temperature is low, and that the tunneling matrix element and the density of states of the tip are constant over the energy range of interest. Then to the extent that these conditions hold, the current has the simple rule:

\[
I \propto \int V \, LDOS_s(V, 0)
\]  \hspace{1cm} (2.4)

Where \(LDOS_s(V, 0)\) is the local density of states at voltage \(V\) relative to the chemical potential, located at the center of the tip. See Fig. 2.2 for a cartoon of how tunneling works in this case.

Of course, these approximations might not hold in the lab. Different bands, or states within the same band with different momenta in the z-direction, will have different tunneling matrix elements. The tip density of states is typically flat for a pure metallic tip, as is used in the research presented here, but can quickly become strongly dependent on energy if the tip is contaminated with atoms from the sample. The tip geometry is not always round, nor the tip wavefunctions s-wave. All topographic and spectral data from STM studies should be assumed to have difficult to quantify measurement uncertainties related to these factors.

### 2.2 Topography and Spectroscopy

The typical measurement from STM is the topograph, in which the tip traces out a surface of constant tunneling current. Theoretically, this data is somewhat awkward, because rather than measuring the local density of states, or even the local density of states integrated from the Fermi energy to the bias voltage, it measures the height at which the integrated local density of states passes some arbitrary set point. However, turning off the feedback loop while scanning over the surface is usually impractical – step edges, adatoms,
vibrational noise, curvature of the surface, and nonlinearities in the piezoelectric actuators all provide strong incentives to keep the feedback loop turned on to keep the tip from crashing into the surface.

The other most common measurement is spectroscopy (scanning tunneling spectroscopy, or STS). By holding the position fixed and sweeping the voltage, we can obtain the tunneling spectrum for that position on the surface. Because the current is approximately proportional to the integrated local density of states, we can find the approximate density of states by taking the derivative of the current with respect to bias voltage. This derivative is usually done via lock-in amplifier, rather than by numerically differentiating an I-V curve. The lock-in amplifier is a useful piece of electronics that measures the amplitude of only a specific frequency component of a signal. It’s used to measure the derivative by adding a small oscillation to the bias voltage, and then measuring the amplitude of that frequency of oscillation in the current signal (see figure 2.3).

The spectrum recorded by STS shows peaks and valleys that can correspond to gaps, bands, Van Hove singularities, etc. The energy precision is mainly limited by thermal broadening, which is approximately
3.2 $k_B T$\cite{65}. The conductance precision is mainly limited by our confidence in the flatness of the density of states of the tip – for a pristine metallic tip, spectra are typically reproducible, but as a tip picks up atoms from the surface the spectra become very unreliable.

2.3 Quasi-particle Interference

By combining scanning and spectroscopy, STM can acquire datasets that measure conductance as function of both energy and position. There are two ways to do this: either by doing repeated scans of the same region at different biases, while collecting dI/dV information with a lock-in amplifier (colloquially a “topomap”), or by taking spectra at each point in a grid over that region (a “dIdV map”). Because both methods use STM to position the tip relative to the sample, they are made at a surface of varying height above the sample and therefore introduce an extraneous signal due to the varying height, which depends more on the integrated density of states than the density of states at the bias voltage. A topomap moves the tip differently for each value of the energy, while a dIdV map uses the same height for all bias values.

Both methods have their strengths and weaknesses. Topomaps are usually faster, especially for small
numbers of different bias values, because interesting samples are usually more homogeneous in space than they are in energy, allowing for acceptable signal to noise without spending as much time waiting for the lock-in amplifier signal to settle. They also do a slightly better job at minimizing vibrational noise. However, in our software they cannot completely eliminate blurring due to the motion of the tip, and also have a difficult time measuring the DOS very close to zero bias, or inside the gap of a semiconducting sample. In practice, we tend to put more time into taking high-quality dIdV maps than topomaps.

By using the combined energy and positional data, we unlock the ability to measure Bloch states in k-space. Early efforts in this direction used measurements of metals Cu[66] and Au[67]. In both cases, scattering of electrons at a step edge created a real-space interference pattern that modulated the local density of states, which was imaged by STM. The modulations in the LDOS changed wavelength as a function of bias; in the Cu sample, this change was equal to the band dispersion of the Cu(111) surface state (reference to a figure showing the data), although this did not hold in the Au sample.

The technique of measuring band dispersion by measuring the wavelength of standing waves is called Fourier-transform STM (FT-STM), or quasi-particle interference (QPI) measurement[68]. A detailed theoretical treatment of QPI as measured by STM is somewhat complicated, but it can be heuristically thought of as follows: an impurity scatters a quasiparticle from some initial state (wavevector \( k_i \)) to some final state (\( k_f \)) without randomizing the phase. The initial and final wavefunctions interfere, creating a modulation (a Friedel oscillation[69]) with wavevector \( q \equiv k_i - k_f \) in the local density of states. Real samples (at least, more complicated than step edges on Cu and Au) can have many scattering sources, each scattering to a superposition of states rather than just one state. In order to extract the modulations, then, we take the Fourier transform of \( dI/dV(r) \).

This intuitive picture of QPI makes it easy to predict the Fourier transform of \( dI/dV(r) \) if the band structure is known. Simply find all the possible scattering vectors (“q-vectors”) between states at a constant energy, and plot the density of q-vectors on a 2-dimensional plot. Equivalently, we can take the autocorrelation of the spectral function \( A(k, \omega) \). (See figure 2.4.)

As the collected image of \( dI/dV(r) \) is made of pixels, the k-space resolution is equal to \( 2\pi/L \) for image size L. To resolve fine features in k-space we therefore need a large L, which implies a large clean area of sample surface. Most scattering, however, involves states in or near the first Brillouin zone, so the scattering vectors are no larger than a reciprocal lattice vector. Therefore, the size of the Fourier transform in k-space need only include the first reciprocal lattice vectors. This reciprocal size is \( (N/2)2\pi/L \), where \( N \) is the number of pixels in one dimension, or \( \pi/a \) where \( a \) is the pixel size. The resolution therefore does not need to be higher than 2 pixels per atom, much less than that required for clear atomic resolution. The orientation of
Figure 2.4: **Left:** Fermi surface, in blue, consisting of pockets centered on the M points of a triangular lattice. Possible scattering vectors are in red. **Middle:** Autocorrelation of the Fermi surface, where the brightness at each point shows the amount of possible scattering by that vector. **Right:** Experimental data from SnSe$_2$, which shows the same scattering pattern.

The image can also be important, and it should be kept in mind that the k-space image obtained will be periodic, so bright Bragg peaks beyond the first may still be folded into your image.

Noise in the Fourier transform of the conductance map can come from many sources. In Fig. 2.4 right image, there are bright lines, vertical and horizontal with respect to the image. These are the Fourier transform of features with very small width and height. If there is only the vertical line in the Fourier transform, this usually means that the tip has changed during the scan (specifically, changed conductivity due to rearrangement of atoms near the apex), creating a horizontal line across the scan in real space. If there are both vertical and horizontal lines, that indicates single “bad pixels” where the tip suffers from brief fluctuation in conductivity due to the thermal motion of tip atoms in the local electric field. Bluntness of the tip leads to deviation from the spherical wavefunction assumption and can suppress high-q wavevectors, dimming the edges of the image. If the conductance map is taken by scanning the tip over the topography at constant bias, high-q wavevectors are also suppressed, albeit only in the primary direction of motion of the tip, due to blur from averaging the conductance signal. Anisotropic scattering, particularly from step edges or domain walls in the sample, can be reflected in accidental anisotropy in QPI data. And a final large source of noise is height difference between different data points due to setting the height via the constant-current condition at some bias voltage. This re-scales the conductance by a map of how the local wavefunction $|\Phi(z(x))|^2$ depends on height, which is nonlinear and can lead to spuriously over- or under-weighting different parts of the scan, particularly near defects or bound states.
2.4 Drift Correction and Strain Measurement

Figure 2.5: (a): Topography on Pb_{1-x}Sn_{x}Se, with characteristic drift due to piezo hysteresis at the top of the image. (b): Fourier transform of (a), highlighting the distorted Bragg peak due to drift.

The function from the piezo voltages to the tip position is not an ideal linear relation, but a complicated combination of nonlinearities, hysteresis, and thermal drift. In light of this, even a perfectly uniform atomic lattice will not result in a uniform image (as recorded data ultimately locates pixels by piezo voltage) (see figure 2.5). This creates problems for measurements both in real space and in reciprocal space. Lawler and Fujita et al.[70], in the process of searching for signatures of nematicity, adapted a lattice-correction algorithm from transmission electron microscopy to STM data to correct for this distortion.

The method works as follows: the lattice is assumed to originally be an ideal lattice, distorted by a slowly-varying displacement field u(r). If we approximate the lattice by its lowest-order Fourier components, the ideal lattice is $A_1 e^{ik_1 \cdot r} + A_2 e^{ik_2 \cdot r} + \text{(other terms)}$, and the distorted lattice is $A_1 e^{ik_1 \cdot (r + u(r))} + A_2 e^{ik_2 \cdot (r + u(r))} + \text{(other terms)}$. To the extent that this approximation holds, if we multiply the lattice by $e^{-ik_1 \cdot r}$, this leaves behind the slowly-varying term $e^{ik_1 \cdot u(r)}$, plus other rapidly-varying terms that can be averaged out over some length scale. Similarly, if we multiply by $e^{-ik_2 \cdot r}$ and average, we find $e^{ik_2 \cdot u(r)}$.

From these, $u(r)$ is eventually deduced.

This method makes no distinction between actual or apparent displacement of the atoms. Thus if the sample is strained, this method can be used to measure that strain, provided that the drift due to piezo hysteresis etc. is small and the smoothing length scale is smaller than the length scale of the strain.
Measurement of strain in this way is due to the work of Dan Walkup, who inducted me into the lab in BC. If the strain is periodic, as in a thin film with lattice dislocations such as in SnTe[71] or FeSe (in this thesis), by scanning a large region it is possible to subtract a low-order fit from the deduced $u(r)$, which hopefully removes drift and allows for quantitative strain measurement.

In addition to measurement of strain, the Lawler-Fujita drift correction algorithm is also useful for reduction of noise in the analysis of STM data. It improves the clarity of the signal in FT-STS images, and, if it is working correctly, also clarifies the lattice position of defects by un-distorting the surrounding lattice.

2.5 Appendix: Tip Etching and Preparation

One of my projects was to refine our process for the etching of the sharp tips for STM, specifically etching tips of high-purity chromium. Therefore we can include an unusually detailed explanation of the tip etching process used for the tungsten tips that were universally used in the experiments reported here.

Most STM tips are made by electrochemical etching of W or Pt-Ir wire [72][73]. For some purposes, however, other materials are required. For example, spin-polarized STM (SP-STM) uses a spin-polarized tip to get spin information about states on the surface of the sample. Ferromagnetic tips can be made with Fe, Ni, or Co, while antiferromagnetic tips can be made with Mn alloy or Cr [74][75]. Cr especially is a good choice of tip material for SP-STM [76]. A typical tip-etching method is to start with a clean piece of wire and then etch away at only a localized region of it, until it forms an extremely thin “neck” that pulls apart under tension [74]. We instead use a method of tip preparation that doesn’t require any steps to localize the etching, trading off ease and simplicity against somewhat lower reliability.

Electrochemical etching, to give a short overview, involves putting two electrodes into an etchant solution. When voltage is applied between the electrodes, this typically drives a chemical reaction at the anode (the side connected to a positive voltage and so accepting electrons, somewhat counterintuitively) where the metal to be etched gets oxidized to a negative ion that is soluble in the etchant. For tungsten, this chemical reaction looks like $\text{W(solid)} + 8 \text{OH}^- \rightarrow \text{WO}_4^{2-} (\text{aqueous}) + 4 \text{H}_2\text{O} + 6 e^-$. For the $\text{OH}^-$ to be available for this reaction, and to increase the solubility of the metal oxide anions, the etchant solution should be a strong base - we use 4M NaOH solution.

In contrast with complicated etching geometries designed to localize the etching, it also suffices to just submerge the whole end of the tip wire, as in Fig. 2.6. What you will observe is that at low etching voltage the submerged wire just etches away uniformly, getting thinner until disappearance, while at high etching voltage the wire is quickly shaped into a blunt hyperboloid that shrinks without ever sharpening sufficiently.
However, there is a middle region (for tungsten, about 1.8 V) where the wire will get thinner and then shrink rapidly from the end, staying sharp during this time as long as the apex angle of the tip is sufficiently small.

We model this by considering etch rate as a function of local radius of curvature. The tips produced at lower voltage were long and thin because the etching only weakly depended on radius of curvature and so the wire didn’t deviate much from its cylindrical profile, while at high voltage all regions of high curvature were etched away. The most important mechanism is diffusion-limited etching [77][78], where curved regions etch faster simply because the reactants can get in and out faster. There are perhaps some additional considerations from the effect of geometry on electric field, and the rate of secondary chemical reactions such as the temporary formation of metal hydroxides.

We numerically simulated the tip etching process, using a lowest-order approximation for the local mass etching rate in terms of inverse radius of curvature, $p_{\text{etch}} = p_0 (1 + r_1 / r_c)$. $r_c$ is the local radius of curvature, and $r_1$ is a free-parameter length scale. For the shape of the tip, $p_0$ is irrelevant. The simulation was coded in Python, using a simple stochastic model with a discrete approximation of local radius of curvature. We simulated a 0.3 mm diameter wire with 1.5 mm "submerged," divided into voxels 0.006 mm per side. Although this model cannot reproduce the nanoscale detail at the apex of the tip, it can replicate the macro-
Figure 2.7: Simulated tip etching for etching probability per exposed voxel per timestep \( p_{\text{etch}} = 0.12 \cdot (1 + 0.175 \text{mm/r}_c) \). Initial wire geometry is a 0.3 mm diameter cylinder with 1.5 mm “submerged.” Snapshots are labeled by their total etching rate as a percentage of maximum etching rate.

scale etching we observe. Based on both geometry and cutoff current, assuming that there’s a proportional correspondence between current and rate of electrochemical etching, our sharp etched tips correspond to a value of \( r_1 \) of approximately 0.175 mm. In Fig. 2.7, you can see the simulated etching trajectory of the tip for \( r_1 = 0.175 \text{mm} \), indexed not by time but by total etching rate as a faction of maximum total etching rate.

We also developed an etching method for Cr tips, using an aqueous etching solution with 0.35 M sulfuric acid and 0.14 M chromium (III) sulfate hydrate (\( \text{Cr}_2(\text{SO}_4)_3\cdot12\text{H}_2\text{O} \)). For this method, the chromium is actually dissolved as a positive atomic ion in the 3+ oxidation state, closely shielded by the sulfate anions. We have scanning electron micrographs of the apex of these tips etched at different voltages in Fig. 2.8. These images aren’t entirely representative of the shape of tungsten tips because the chromium etching process etches along the crystal planes of the metal more preferentially than the tungsten etching process does, and so we expect the tungsten tips to be more uniform given similar sharpness.

After the tip is made, it is cleaned and transferred into the vacuum chamber of the STM. It is now contaminated with surface oxide from being exposed to air, so the surface oxide is removed by vacuum heat treatment, using e-beam heating. A hot filament is brought close to the tip, and high voltage is applied to induce electrons to be emitted from the filament, get accelerated by the voltage, and then impact the tip, depositing their energy and heating the tip to above the decomposition temperature of the oxide but below the melting temperature of the metal. For tungsten, we use a small white-hot filament approximately 5 mm from the tip and apply a high voltage of 1000 V, leading to a 2 mA emission current that heats the tip above
800 °C (orange-hot) for 3 to 5 minutes.
Figure 2.8: SEM images of the apexes of etched Cr tips, with scale bars. a: Etching voltage of 3.3 V, b: 3.1 V, c: 2.9 V, d: 2.5 V
Chapter 3

Molecular Beam Epitaxy

3.1 Overview

Molecular Beam Epitaxy (MBE) is a technique for growth of layered materials, developed by Arthur and LePore at Bell Labs[79][80]. By slowly depositing atoms in ultra-high vacuum, thickness and composition can be controlled down to the sub-layer scale, which makes it ideal both for growing single-layer materials and for growing layered heterostructures.

An MBE system typically consists of a vacuum chamber, sample stage, evaporation sources for different elements or compounds, quartz crystal microbalance (QCM) thickness monitor, and surface probe such as reflected high-energy electron diffraction (RHEED).

Figure 3.1: Cartoon schematic of a simple MBE.
3.1.1 Vacuum

As the name implies, molecular beam epitaxy relies on the mean free path of the atoms being longer than the size of the chamber, so that the material to be deposited travels from the source to the sample in a straight beam. The mean free path \( l = \frac{1}{\sigma \rho_n} \), where \( \sigma \) is the scattering cross-section and \( \rho_n \) is the number density of particles. A typical value for the cross-section is \( 6.6 \cdot 10^{-20} \text{ m}^2 \) (for an effective diameter of 0.29 nm)[81], and this implies that even at a pressure of \( 10^{-4} \) Torr, at which an ideal gas has a number density of \( 3.2 \cdot 10^{18} \) particles per cubic meter, the mean free path is tens of meters long. So mean free path is actually not a stringent constraint. The real constraint on vacuum quality is the Langmuir timescale at which the gas atoms in the chamber impact the growing sample - we want to minimize the incorporation of oxygen and nitrogen into growing films. One Langmuir is \( 10^{-6} \) Torr-seconds, and it is the approximate amount of flux necessary for a surface to adsorb a layer of gas from the vacuum. If we want to grow as slowly as 1 minute per layer, and we want less than 1 percent of a Langmuir during that minute, this requires a base pressure (or at least a base partial pressure of reactive species) of about \( 2 \cdot 10^{-10} \) Torr.

This vacuum is typically provided by a turbopump, which can reach base pressures as low as \( 5 \cdot 10^{-10} \) Torr, though it’s also possible to pump the chamber using an ion pump or other UHV pump. Such high vacuum also implies a chamber construction of stainless steel parts sealed with copper gaskets. Moving parts are controlled by mechanical feedthroughs using flexible bellows or magnetic couplings, and the inside can be looked at through viewports that can be shuttered from the inside to avoid being coated during deposition.

An important vacuum technique, which I would be remiss not to mention, is baking. After being exposed to air, the interior surfaces of the vacuum chamber will adsorb a layer of gas molecules, mostly water vapor. Once pumping begins, the gradual desorption of this layer is a major source of gas in the chamber, supplying up to \( 10^{-8} \) Torr over a long period. To remove this problem, after exposure to air the walls of the chamber should be heated up to accelerate the removal of this gas - hence “baking.” We wrap our chamber in electrical heating tape and insulate it with aluminum foil, raising the temperature to above 100°C (and less than 120°C due to selenium’s low evaporation temperature) for several days.

3.1.2 Sample stage

The sample stage and sample holder contain several key decisions for design of an MBE chamber. Heating, temperature sensing, sample geometry and other considerations all need to be taken into account.

Because the growth dynamics of materials change as a function of temperature, we want precise control over the temperature of the sample, typically within the range of 150 to 500°C. We also might want to access temperatures in excess of 600°C to anneal the substrate crystal to make it flatter, remove the oxide
layer from a reactive substrate such as silicon, or for other reactions like graphitizing the surface of silicon carbide[82]. The best method for fine control of temperature is radiative heating, and the two options for reaching higher temperature are e-beam heating and direct-current (DC) heating.

Radiative heating just means locating a filament behind the sample, and running current through the filament to heat everything nearby. E-beam heating uses the thermionic emission from that same hot filament, and by applying a high voltage between the filament and sample uses the emitted electrons to deliver more energy to the sample, more directly. This requires the sample to be conducting to avoid charging; or if the sample is not conducting, its back side should be coated with a metal such as tungsten. Because thermionic emission scales exponentially with filament temperature and becomes appreciable only at white-hot filament temperatures, e-beam heating has a minimum temperature that is near the maximum temperature for radiative heating, and a much higher maximum temperature. It is also less temperature stable than radiative heating, again because of the exponential dependence on filament temperature, which amplifies small variations and feedback effects.

DC heating runs a current directly through the sample to heat it via joule heating - this works best with semiconducting substrates. DC heating has less spatially uniform temperature than radiative heating because the change in resistivity as a function of temperature leads to hot spots, particularly if the substrate is shaped irregularly. However, with proper calibration it’s possible to go from low to high temperatures without turning on or off high voltages. For the chamber designer who wants to allow for the options of either e-beam heating or DC heating, it’s necessary to have two electrical contacts capable of transmitting up to 10 A, which can be isolated at up to 1000 V relative to a third contact.

There are two main options for measuring the temperature of the substrate, thermocouple and pyrometer. Thermocouples sense the temperature at a specific junction in a wire, and so if your route a thermocouple close to the sample you can sense the temperature at that location in real time. Pyrometers infer the temperature of a material from the spectrum of emitted radiation, and so if you have an infrared-transparent window that points directly at your sample, and it occupies enough of the field of view, you can sense its temperature.

Both real-time methods suffer from systematic errors: the thermocouple cannot be located directly at the growing sample, and the pyrometer can pick up light from non-substrate sources and also needs to be calibrated with the emissivity of the substrate. To perform calibration, perhaps the best way is to use a sacrificial substrate with a thermocouple attached directly to its surface with thermally conductive adhesive - we have a separate chamber specifically for this task.

The size of our samples is set by their intended use, and typically doesn’t require more than a 3x3 mm
area. For STM, the coarse range of motion over which we can move the tip extends to 2-5 mm, depending on the system. For STMs with no optical access, where there’s uncertainty about the location of the tip, it’s better to choose a sample size such that the sample covers the whole range of motion. RBS, which we use to measure the composition of our samples, has a 2 mm spot size, which is another factor constraining the size of the sample. In our case, the standard sample holder for STM is more than large enough for our purposes.

To use RHEED, the sample needs to be level and have an unobstructed side view in one direction. This is solved by holding the substrate down with two parallel clamps, and aligning the clamps such that the RHEED beam shines across the sample in between them.

### 3.1.3 Sources

The atomic or molecular sources used in molecular beam epitaxy need to have a stable rate even at very low flux. The typical method to do this is to use a Knudsen cell[83] (K-cell), but different materials might work better with e-beam heating of a solid rod, DC heating of an elemental filament, heating a salt to release a volatile component, or other methods of delivery. Since only K-cells were used in the preparation of materials in this thesis, I will give a brief overview of their properties and operation.

Knudsen cells are based on the science of evaporation and effusion, which was described by Hertz, Knudsen, and Langmuir[84]. Hertz and Knudsen separately measured the evaporation rate of mercury in vacuum, and determined that the evaporation rate per unit area is proportional to the saturated pressure at that temperature, divided by the temperature.

\[ M \propto \frac{p(T)}{T} \quad (3.1) \]

In the Hertz-Knudsen equation, Knudsen gives the constant of proportionality as \( \alpha \frac{\sqrt{2}}{4\pi R} \), where \( R \) is the gas constant and \( \alpha \) is some constant less than 1, which depends on the geometry and the surface impurities. Simultaneously, Langmuir showed that the same relationship also held for evaporation from solid surfaces[85].

The original Knudsen cell was a heated box, with gas at its equilibrium pressure inside, with a pinhole opening. This makes a sort of ideal evaporation source with flux per area of the pinhole

\[ M = \frac{1}{\sqrt{2\pi R}} \frac{p(T)}{T} \quad (3.2) \]

where \( p(T) \) is technically the partial pressure difference between inside the box and the outside vacuum.

Effusion from a K-cell follows a cosine law[86], just based on the geometry of the opening as seen from a
varying angle. It is therefore important to point the K-cell (as given by the normal vector of the opening) toward the sample, so that the rate of deposition is as constant as possible across the sample.

What we call “K-cells” in modern terminology are not boxes in internal equilibrium, but are long cylindrical crucibles (those used in our system are alumina, but pyolytic boron nitride is another common material) with the material to be evaporated at the bottom. The relatively large size of the opening reduces the evaporation rate per unit area to something in between the maximum rate and the Hertz-Knudsen equation parameterized by $\alpha$. It also narrows the angular distribution, concentrating deposited material on those angles that have direct line of sight to the source material.

### 3.1.4 Quartz Crystal Microbalance

With the many factors that can affect deposition rate, it’s important to be able to measure it experimentally. The most common way to do this is with a quartz crystal microbalance (QCM). Quartz is a piezoelectric material, and so it flexes when an electric field is applied to a deposited electrode - and conversely, flexing of the quartz will drive a voltage in the electrode. With a sinusoidal driving voltage, it’s possible to drive vibrations in the crystal and sense the resonant frequency via the impedance of the crystal. G. Z. Sauerbrey [87] determined how to use shifts in the resonant frequency to measure the thickness of the deposited film. With proper setup, precision of 0.1 Å is easily achievable.

In practice, we use small disks of quartz, bought with specialized electrodes already deposited, that are what is called “AT-cut,” which is an angle of cut relative to the crystal axes that provides temperature stability and encourages vibration in the thickness-shear mode. Temperature variability is still an issue though, especially when hot K-cells are radiatively heating their surroundings, and so water cooling of the QCM is often desirable.

The measured thickness depends nonlinearly on the frequency shift, depending both on the density of the deposited film and on its shear modulus. The relationship is:

$$
\Delta t = \frac{N_q \rho_q}{\pi \rho_f Z f_L} \tan^{-1}\left(Z \tan\left(\pi \frac{f_U - f_L}{f_U} - \frac{f_L}{f_U}\right)\right)
$$

where $\Delta t$ is the change in thickness, $N_q$ is the frequency constant for AT-cut quartz, $\rho_q$ and $\rho_f$ are the densities of quartz and the deposited film, $Z$ (found in tables of “Z factors” for different materials) is equal to $\sqrt{\frac{\mu_q}{\rho_f \mu_f}}$ ($\mu_q$ and $\mu_f$ being the shear moduli of quartz and the film)[88].

It is also important to consider geometry. If the QCM could be located exactly at the sample, the measured deposition rate would be close to the flux incident on the sample. But if there is some offset,
this leads to a tooling factor that can be different for different sources. This can be calibrated directly by depositing a thick layer of one material and measuring the thickness via profilometer.

### 3.1.5 Reflected High Energy Electron Diffraction (RHEED)

Electron diffraction is an extremely popular surface probe that gives information about the structure of a substrate’s or sample’s surface. Importantly, it can even be used during the growth process itself, to monitor the growth in real time. Reflected high energy electron diffraction (RHEED) uses a high angle of incidence, nearly parallel to the surface, to ensure a low penetration depth and high surface sensitivity. Because of the high energy relative to the surface phonons, reflection are very elastic even at high temperatures.

The diffraction pattern produced by RHEED typically looks like vertical streaks within a semicircle. Three things are needed to explain this: the Laue diffraction condition, the low penetration depth, and the finite domain size on the surface.

The Laue diffraction condition is that the wavevector of the scattered electron should differ from that of the incident electron by a reciprocal lattice vector of the thing it’s scattering off of. Of course, the energy also has to be conserved. A common construction to visualize this is the Ewald sphere, which is the sphere in reciprocal space of scattering vectors that conserve energy. Zero must obviously be included in the Ewald sphere, as it is a scattering vector that conserves energy, and so should the scattering vector $-2k$ that reflects the incident electron back in the opposite direction. It's therefore intuitive that the Ewald sphere is a sphere of radius $k$ centered at $-k$ (often simplified to $k$ by symmetry). Where reciprocal lattice vectors intersect the Ewald sphere, the Laue condition is satisfied and we see scattering at those scattering vectors.

Because of the low penetration depth, the reciprocal lattice points are elongated into rods in reciprocal space. This is because the electrons only see the very top few atoms in real space, and when translating into reciprocal space we take the Fourier transform of this thin slice to get a broad distribution of reciprocal vectors. Finite domain size of the sample acts in the same way (if to a lesser degree), giving the reciprocal lattice points a finite thickness. So after accounting for finite size of the scattering atoms, there are many more allowed scattering vectors - rather than only the reciprocal lattice points, there are now long rods of finite thickness located at each reciprocal lattice point.

Imagining the Ewald sphere again, the updated condition is that wherever these rods intersect the the Ewald sphere, we see scattered electrons. Viewed from high angle of reflection, as it must be in order to capture a high intensity of these reflected high-angle-of-incidence electrons, these intersections appear as streaks, which resolve into points in the limit of large domain size and low surface roughness on the sample.

Another feature of RHEED patterns is Kikuchi lines[90]. These are lines connecting the diffraction
maxima, and are due to inelastic scattering. Seeing pointlike diffraction spots and Kikuchi lines is possible on annealed substrates, but is uncommon on films grown by MBE, which tend to be rougher and have smaller domain size than the underlying substrate. Instead, information about the surface is gained by looking at the spacing between diffraction maxima and their broadness. For epitaxial layer-by-layer growth, it’s possible to count “RHEED oscillations” as the surface gets rougher and then smoother again as each layer is partially finished and then completed.

3.2 Growth Mechanics

The process of growth begins after the substrate is loaded into the vacuum chamber in its sample holder, and both sample holder and sources to be used are degassed (heated to above the intended operating temperature to remove adsorbed gas) and returned to their intended operating temperatures. Shutters over the sources are opened, directing their respective fluxes towards the substrate. The shutters are closed and the deposition stopped after a set amount of time, or by watching RHEED oscillations for some highly epitaxial samples.

On the surface of the sample, the growth dynamics are set by four rates: the source atoms’ or molecules’ rate of sticking to the surface (physisorption), their diffusion around the surface, their re-evaporation (desorption) rate, and their chemical bonding into larger parts of the film (chemisorption).

The sticking rate is not just equal to the incident flux, it also depends on the strength of the various
intermolecular forces between the sample or substrate and incident atom or molecule, which tend to be strongest for polar or highly polarizable molecules on polar substrates, on the temperature, and on the coverage of the layer so far [91]. Re-evaporation is essentially just the reverse of physisorption. When the chemisorption rate is small relative to the sticking rate, this is in a balance with the re-evaporation rate, which is typically studied in the literature in terms of the surface coverage as a function of partial pressure[92].

Once adsorbed, atoms or molecules diffuse around while remaining bound to the surface. The typical model of this is classical surface diffusion, which approximates the hopping frequency as $\Gamma = \nu e^{-\frac{\Delta}{k_B T}}$, where $\Gamma$ is the hopping frequency, $\nu$ is some effective combination of vibration frequency and thermalization rate, and $e^{-\frac{\Delta}{k_B T}}$ is the Boltzmann factor for overcoming an inter-site barrier of size $\Delta$.

The chemisorption rate, once concentration and diffusion rate are accounted for, depends on the kinetics of the chemical reaction between different species to form an epitaxial layer. This rate has an overall scale set by the particulars of the chemical reaction intended to produce the sample, but in general also increases with sample growth temperature. However, although chemical reaction rate increases with temperature, the temperature also controls what compound, stoichiometry, or crystal structures are stable, and what their free energy is. In order to grow a particular compound in a particular structural phase, you may have to control the temperature to within $40^\circ C$, because if the temperature is too low the same atoms will form a different compound, and if the temperature is too high then the thin film will become unfavorable altogether and undergo thermal decomposition.

Another important factor is that elements do not necessarily evaporate as lone atoms, but often evaporate as small clusters. This is particularly true for chalcogenides, which predominantly evaporate as species like $\text{Se}_6$ or $\text{Te}_4$ [93][94], unless exposed to a high-temperature “cracking” filament. These clusters are less reactive than free atoms, increasing the flux needed for the same effective contribution to the reaction rate.

These details of the growth process mean that often the calibration with the QCM is inaccurate. Different atoms or molecules might have different rates for all of the above processes, and so in order to produce a stoichiometric film, the incident flux must be non-stoichiometric. The necessary corrections are usually determined by trial and error. One situation where the problem is simpler is for films with only two types of atom. The species with a higher re-evaporation rate can be deposited in excess, on the assumption that whatever can react with the other species, will react, and the left-over material will be re-evaporated.
Figure 3.3: Cartoon of the different processes contributing to growth. A cluster of atoms (green) is adsorbed (a), migrates around the surface with some lifetime before desorption (b), or reaction with the growing film (c).

3.2.1 Film Morphology

As films grow, their overall morphology is typically classified into one of three types: flat layer-by-layer growth (Frank-van der Merwe [FM]), growth in isolated islands (Volmer-Weber [VW]), or growth that starts out layer-by-layer but eventually becomes dominated by islands (Stranski-Krastanov [SK]) [95]. VW growth happens when the film doesn’t wet the substrate, and is pulled together by surface tension into islands - this is typically avoided by substrate choice and preparation. FM growth is the ideal growth mode for most purposes, but relies on lattice constant matching between the substrate and film. SK growth is more typical, starting out smooth but accumulating islands as they have the opportunity to nucleate, or as the film is forced to fracture into islands to relieve strain [96].

For layered materials such as those studied in this thesis, it’s also important to note that growth happens primarily at the edges of a layer. This has several consequences, the main one of which is to suppress the growth of islands from simple nucleation sites, because rather than growing in all directions, a small defect will just seed a new layer, which will then grow horizontally at its edges. By looking at the morphology of a film where this dynamic is present, we can make inferences about the rate of nucleation of new layers, versus the growth rate at the edges of existing layers. In order to grow tall islands, the islands either need to be a different compound than the rest of the film, or the islands need to be oriented such that the edges of the layers are tilted relative to the plane of the substrate, which requires a large defect.
Another consequence of growth happening at the edges of a layer is the importance of screw dislocations. If there is no screw dislocation in a layer of a growing film, then the growth of the next layer has to wait on the nucleation of islands on the next layer. However, screw dislocations constantly have exposed edge, avoiding this potential bottleneck. Thus in films with high rate of edge growth relative to the nucleation of new layers, the morphology can become dominated by spiraling growth centered on screw dislocations.

After the growth finishes, there is typically a period of annealing of the film, which means heating it in vacuum with no incident flux, typically for a long time relative to the growth time. Annealing can reduce the concentration of defects, change the morphology, and change the stoichiometry. As the film is growing, metastable defects may become incorporated into it, and annealing can help to heal these defects and reach a lower free energy state. Changes to morphology follow this same principle, where if atoms are mobile enough, morphology that was dictated by the kinetics of growth can get rearranged to lower the free energy cost of the film - this is done intentionally when the minimum free energy is for a flat film. Changes to
stoichiometry of the film occur when a high vapor pressure species undergoes evaporation directly from the film - in this case, annealing can be done to control the composition of the final film, or even to deliberately introduce defects at the sites of the missing atoms.

3.3 Home-built MBE

The samples studied in this thesis were grown in a miniature MBE chamber designed and built by me. It has three sources, a turbopump, QCM, high voltage electrical feedthroughs, and other necessary vacuum paraphernalia. The original plan for this chamber was to attach it directly to the STM, to be able to rapidly grow and learn from samples. This was tried for several months, but eventually the chamber was split off due to the wait time when using the turbopump, sample holder problems that would only get resolved later after machining new parts, and concerns about selenium contamination. We’ve learned enough lessons to be able to successfully implement a combined STM-MBE system if we ever re-develop the need to.

Figure 3.6: CAD model of the mini-MBE.

With the MBE not directly connected to the STM, we need some way to transfer samples while leaving them pristine. For this, we use a custom vacuum shuttle (also called vacuum suitcase) system. This is a small independent vacuum chamber that consists of just a small four-way cross of stainless steel with attached magnetic manipulator, gate valve, and vacuum pump, which is a small combined ion pump and
non-evaporable getter pump. When the gate valve it holds vacuum of better than \(1 \cdot 10^{-9}\) Torr, and can be moved between the MBE and STM without exposing the sample inside to air. In order to get the sample into or out of the vacuum shuttle, the other side of the gate valve is connected to an interstitial space that can be pumped down to ultra-high vacuum. This interstitial space is attached to the STM vacuum chamber via a second gate valve, and when the vacuum is sufficiently good, both gate valves can be opened to allow sample transfer into or out of the vacuum shuttle. This is a highly reliable way to move samples from MBE to STM chambers, which we have carried out many times without seeing surface contamination as a result of the transfer process.

The sources of the custom mini-MBE make an angle of \(23^\circ\) relative to vertical, and are approximately 4 in from the substrate during growth. The effective substrate size is at most 3.5 mm. Using these dimensions, we can estimate the inhomogeneity of flux in this system due to the growth geometry. The two relevant factors are an angular factor due to the flux dropping off away from the center of the beam, and a \(\frac{1}{r^2}\) factor due to distance. The maximum total difference in flux between parts of the substrate is therefore expected to be

\[
\cos(tan^{-1}(\frac{\cos(23^\circ) \cdot 3.5 \text{ mm}}{4 \text{ in}})), \frac{(4 \text{ in})^2}{(4 \text{ in} + \sin(23^\circ) \cdot 3.5 \text{ mm})^2}
\]

or a factor of 0.97. We can therefore expect different parts of the sample to be very similar to each other in elemental composition.
Chapter 4

SnSe$_2$

After reports of superconductivity in monolayer SnSe$_2$ on graphene\cite{98} and graphite\cite{99}, we grew SnSe$_2$ on graphite in our own MBE to explore its properties. Although we saw the same gaps in DOS as previous groups, this material didn’t have superconducting behavior under external magnetic field. We show using quasiparticle interference that even the bilayer film has an avoided crossing 10 meV below the Fermi energy. Another hint is that the monolayer film has a strong Moiré pattern due to coupling to the underlying substrate, and the gap size depends (non-monotonically) on the twist angle.

Figure 4.1: Top and side view of SnSe$_2$ structure, using dashed and wedged bonds to denote bonds in and out of the page.
4.1 Introduction

Recently, there have been two separate reports that monolayer SnSe$_2$ grown on graphene or graphite is a superconductor, both based primarily on scanning tunneling spectroscopy. Y. Mao et al. (2017) grow SnSe$_2$ on crystalline graphite and take spectra showing a large gap of 15 meV and estimate a $T_c$ of 25 °K [99], which would be practically a high-$T_c$ superconductor. Y. Zhang et al. (2018) grow SnSe$_2$ on several-layer graphene and find a gap of 0.9 meV, and estimate a $T_c$ of 4.8 °K [98].

Tin diselenide is a metal dichalcogenide primarily studied for its optical absorption properties [100], [101]. In bulk form it’s an n-type semiconductor with bandgap 0.97 eV [102]. Looking at density field theory (DFT) calculations of the band structure (Fig. 4.2), we expect to see the conduction band opening up gradually at the M point in the Brillouin zone [103]. SnSe$_2$ grows as a layered material, each layer being a triangular lattice (lattice constant 0.38 nm) of Sn atoms bonded together by Se atoms above and below (see Fig. 4.1). In bulk it tends to grow with the 1T structure (”ABC” stacking of a triangular lattice, rather than ”ABA” stacking). Tin has stronger spin-orbit coupling than most first and second row transition metals because of its high atomic number [104], which puts SnSe$_2$ in a similar class as transition metal dichalchogenides, which have a variety of unusual electronic properties [105].

Upon electron doping, either by intercalation with donor metal complexes [106], [107], [108] or gating with a strong electric field [109] SnSe$_2$ can become a superconductor with $T_c$ of up to 6 °K and upper critical field $H_c$ of up to 0.9 T. There have also been reports of superconductivity induced by high pressure [110] and by growing a highly strained single layer on STO(111) [111], with similar $T_c$ but $H_c$ of 2.5 T and 5 T respectively, suggesting higher carrier density. Zhou et al. [110] also argue that the critical field as a function of temperature is a better fit for p-wave superconductivity.

In order to investigate the origins of the reported gap in the density of states, we grew monolayer SnSe$_2$ on graphite. We replicated the observations of both Mao et al. [99] and Zhang et al. [98], measuring two gaps / pseudogaps. But in measurements in a perpendicular magnetic field of up to 9 T, neither gap closed as we would expect of a superconducting state.

Being monolayers, our samples were heavily affected by their interface to the underlying substrate. Different electron affinities between the substrate and the sample will lead to doping of the sample. Mismatch in lattice sizes will lead to strain [112]. There can also be interchange of phonons and mobile electrons between the substrate and the film. The SnSe$_2$ work function is approximately 5.05 eV [113], while the graphite work function is approximately 4.48 eV[114], and so the graphite will be the electron donor.

During measurement, we noticed Moiré patterns indicated that different domains of the film had different angles relative to the substrate. These different domains also had different gap sizes. The electronic
properties of twisted systems are the subject of current interest, primarily twisted bilayer graphene [115] but also heterostructures such as molybdenum disulfide on graphite [116]. Moiré patterns change the electronic structure by increasing the effective size of the unit cell, shrinking the Brillouin zone and providing an interaction mechanism for electrons that were previously in neatly-separated momentum states. In bilayer graphene, this effect, in combination with interlayer coupling, dramatically changes the shape of the electron bands even with a relative twist of 1 degree. However, for the case of SnSe$_2$, it’s possible that the simple model of a 2D potential suffices to get a handle on the observations.

If we decompose our single-particle wavefunction into Bloch states, in the form $\Psi(k, x) = u(x)e^{ik\cdot x}$, a Moiré pattern provides a periodic potential $\Delta H = \sum_j a_j (e^{ij\cdot x} + e^{-ij\cdot x})$ that has zero expectation for all pure crystal momentum states, but splits degenerate states that are separated by $2j$. The nonzero $a_j$ components, i.e. the periodicities of the Moiré superlattice, can be thought about as in e.g. Hermann[117], where the two lattices form a pattern with reciprocal lattice vectors equal to the difference between the reciprocal lattice vectors of the individual lattices. However, a neglected detail is that nonlinear effects in real space correspond to linear combinations of repeated convolutions in reciprocal space. Remembering that if our distributions are collections of delta functions at various vector locations, convolving them just adds all the
vectors \( \int \delta(x - a - t)\delta(t - b)\,dt = \delta(x - a - b) \). Therefore the most visible pattern is allowed to be a higher-order combination of the reciprocal lattice vectors, if that combination has long wavelength at low enough order that it retains a high amplitude.

4.2 Methods

Highly oriented pyrolytic graphite (HOPG) was cleaved in air and then degassed in the mini-MBE at 300 °C for 1 hour. HOPG is a convenient substrate precisely because of its simple preparation - the graphene layers are minimally reactive with air except at edges and defects, which are rare. And although it does degrade slowly in air[114], heating in vacuum can release even chemically bonded gases, primarily by decomposing oxidized sections into carbon monoxide gas. HOPG has a honeycomb lattice with lattice constant 0.246 nm[118], but for STM the honeycomb structure is typically unobservable, and instead we see the triangular lattice of p-orbital electrons that are concentrated in the center of each honeycomb cell.

On this substrate, monolayer SnSe\(_2\) was grown via molecular beam epitaxy. The substrate was warmed to 70 °C, and Sn and Se were evaporated from Knudsen cells at rates of 0.15 and 1.5 Å/min respectively, for 11 minutes. The temperature was then ramped up to 250 °C for 1 hour, driving off excess selenium and annealing the film. Film composition was checked by Rutherford Back-scattering spectrometry (RBS) carried out at the NEC Pelletron accelerator at the Materials Research Laboratory, University of Illinois [119].

After growth, the samples were transferred to a scanning tunneling microscope in a vacuum suitcase with base pressure 5×10\(^{-10}\) Torr to prevent degradation of the sample. STM measurements were performed at and below 4.2 °K in Unisoku STMs, using electrochemically etched and vacuum annealed tungsten tips. \( dI/dV\) spectra were taken using lock-in amplifiers at frequency of 950 Hz. The spectra in Fig. 4.4 are selected single-point spectra, while all spectra in Figs. 4.5 and 4.6 are averaged from line-cuts over 5-10 nm, and are representative.

4.3 Scanning tunneling spectroscopy

The growth process used results in islands of primarily monolayer SnSe\(_2\) composed of multiple crystalline domains, with average domain size of 60 nm. The lattice constant a measured by STM was 3.75 Å, within calibration error of the standard value for bulk SnSe\(_2\) [120]. The step height between graphite and the first layer of SnSe\(_2\) was 1.3 times larger than the step height between further layers.

We replicated the scanning tunneling spectroscopy measurements of both Mao et al. (2017) [99] and
Zhang et al. (2018) [98]. At 4.2 °K, the spectrum exhibits a gap of $\Delta \approx 15$ meV Fig. 4.4a and 4.4b. After cooling to 0.3 °K in a He3 stage, a smaller gap of $\Delta \approx 0.2-0.5$ meV, varying with position, can be resolved. Under perpendicular magnetic field, neither the 10 meV gap nor the 0.5 meV gap change shape with magnetic field, as shown in Fig. 4.5.

Different domains of SnSe$_2$ had different sizes of the 0.5 meV gap, as in Fig. 4.6. No other difference in tunneling spectra could be observed. These different domains were at different angles relative to the underlying graphite, generally centered on 30°, which induced Moiré patterns in the surface. This twist angle is the longest-wavelength possible pattern of these two lattices, indicating that a long wavelength is energetically favorable, likely to allow for minimal deformations of the lattice to maximally increase the Van der Waals interactions between the substrate and film. We did find one domain with an angle of 41 30°, which actually had a strong but very short-wavelength pattern, and a gap of size only 0.20 meV.

The spectra averaged together to produce Figs. 4.5 and 4.6 are not homogeneous, instead exhibiting broad peaks in density of states at different energies – particularly dramatic in Fig. 4.5a compared to Fig. 4.4b due to the spectra in Fig. 4.5a being taken close to a step edge. These features are primarily due to quasi-particle interference (QPI), as well as differences between on-atom and off-atom spectra. SnSe$_2$
4.3.1 QPI and inhomogeneity in spectra

A conductivity map of SnSe$_2$ contains ripples of higher conductivity that move as the voltage is changed. These QPI patterns are the standing waves formed by coherent scattering of quasiparticles. If incoming state with wavevector $\mathbf{k}$ is scattered to state $\mathbf{k}'$, this will contribute to a standing wave with wavevector $\mathbf{k}-\mathbf{k}'$. They cause position-dependent peaks in the spectra as the ripple passes the spectrum location.

Here are two examples of QPI on SnSe$_2$, the first on the bilayer and the second on the monolayer:
In Fig. 4.8a, we can clearly see a wave traveling from right to left with increasing bias voltage. If we take a spectrum on the right-hand side of the field of view, as in Fig. 4.8c, a peak gets added at the voltage where the wave passes, filling up the gap. If we take a spectrum on the left side (Fig. 4.8d), the peak gets added at a different voltage instead.

The QPI affects different parts of the unit cell differently. The spectrum in Fig. 4.8b is on the selenium site and is a representative sample of spectra from that location in the unit cell, while spectra c and d are on the tin site and are different due to the QPI signal. Note that in Fig. 4.8, the selenium atoms show up as diffuse ellipses at positive bias but are in the dark at negative bias, and the bright lines at negative bias are actually over the tin sites. This measurement indicates that the orbitals involved in the bands near the Fermi energy are located closer to the tin atoms.
Figure 4.6: Comparison of spectra on different domains, with corresponding topography. a and b: The largest Moiré pattern corresponds to a $30^\circ$ angle between the SnSe$_2$ and graphite lattices. c and d: $31^\circ$. e and f: $33^\circ$. g and h: $35.5^\circ$.

Figure 4.7: Layers of a 32x32 nm conductance map on primarily bilayer SnSe$_2$. Setup voltage 50 mV. The distinct QPI disperses as bias voltage increases.

We can use this QPI to look at the band structure, as described in chapter on scanning tunneling microscopy. We have two 32x32 nm conductance maps on the region shown in Fig. 4.7, one from -150 mV to +150 mV in 4 mV steps and one from -50 mV to 50 mV in 2 mV steps. Returning to superconductivity for a moment, we should also note that the larger energy scale map was actually taken under magnetic field of 1.5 T, and shows no superconducting vortices, although a Moiré pattern is visible on the single-layer portion of the topography. If we take the Fourier transform it reveals that the coherent scattering vectors, in addition to being at the reciprocal lattice vectors, are also at the vectors connecting the M-points of the Brillouin zone (which will from here on be referred to colloquially as ”M points” or ”M points in q-space”), where DFT calculations lead us to expect the bottom of the SnSe$_2$ conduction band. For an image showing the expected QPI, refer back to Fig. 2.4.

This pocket of scattering vectors at the M points changes in size as a function of energy, which we can
Figure 4.8: a: Layers of a 4x4 nm conductance map, from -0.5 to 0.7 mV. Setup voltage 4 mV. The QPI shown travels from right to left with increasing bias. b: STS spectrum on Se atom in the center of the image. c: Spectrum over a Sn (tin) site on the right side of the image. d: Spectrum over a Sn site on the left side of the field of view.

Figure 4.9: Fourier transforms of the LDOS at slices of constant energy, from the conductance map shown in Fig. 4.7. Color scale is logarithmic in Fourier coefficient, with color scale bounds set "by eye," which is notably scaled by a different factor for the 90 mV energy. Certain impurities have been masked in real space, but the data is not filtered or symmetrized in reciprocal space. The vertical and horizontal lines passing through the center are due to noise with small vertical / horizontal size in real space. The largest bright spot in the center is $q = 0$, the smallest scattering vector. The second-brightest spots in the image, arranged in the large hexagon, are the Bragg peaks, scattering vectors between neighboring reciprocal unit cells. It is only the tertiary spots, located equidistant between the center and the Bragg peaks, that correspond to scattering between two different Fermi surface pockets at the M point of the Brillouin zone. The change in shape of these spots at the M points reflects the change in shape of the Fermi surface pockets.

see by taking radial averages centered on these points. We show a waterfall-style plot (Fig. 4.10) of radial average offset by energy, with some guide lines drawn in to highlight the changes in size. We can see that around -10 meV, one local peak in the radial average is moving away from zero at the same time that another is emerging in the center. This looks like an avoided crossing, a pattern caused by the states from two bands mixing as they get close together in energy and momentum. In a superconductor, we might see this feature centered at 0 V - but the fact that it appears in the QPI of bilayer SnSe$_2$, not centered on the Fermi energy, indicates that there is some interaction that is inducing the formation of a gap even if doing so doesn’t lower
Figure 4.10: Waterfall-style plot of the radial average of QPI intensity around the M points in q-space. The plotted radial averages are averaged from the 10 M-points not overlapping the vertical band of noise, combined from two dI/dV maps of the same area, one from -150 mV to 150 mV, the other from -50 mV to 50 mV. Vertical position of the radial averages is offset such that the mean intensity is mapped to the corresponding energy. Blue lines track local maxima or edges in the radial average.

the electronic energy (which is what would drive the formation of a superconducting gap or spontaneous CDW gap).

This band structure inferred from QPI is at odds with the spectroscopic measurement of local density of states (Fig. 4.11), which suggests that the Fermi energy is close to the top of the semiconducting bandgap. Given the fact that the pocket doesn’t appear to be closing even at -150 mV, and the low density of states, a possibility is that this is a surface states as in MoS$_2$[116], where a Moiré pattern is hypothesized to be the perturbation that creates a small number of states to bridge the semiconducting gap.
4.4 Discussion

The BCS theory of superconductivity provides an approximate relationship between gap size and upper critical magnetic field [121][122]. If the gap has $\Delta = 0.5$ meV, then we expect $T_c$ to be approximately 3.3 °K and the upper critical field to be no more than 6.1 T. This is simply the field at which flipping a magnetic moment of size $\mu_B$ will pay for the pair binding energy. In practice the critical field will be much less, because this upper bound neglects orbital angular momentum and the energy of the field itself that is being excluded by the Meissner effect. Ginzburg-Landau theory relates the critical field to the coherence length ($\xi$) of the superconducting wavefunction, with the relation for type II superconductors $H_{c2}(0) = \phi_0/(2\pi \xi^2)$, where $\phi_0$ is the quantum of magnetic flux. There is an exception if the superconducting wavefunction has p-wave pairing [123], but the density of states will still change under high magnetic field [124]. Additionally, the reports of superconductivity in SnSe$_2$ grown on STO(111) [111] are more consistent with s-wave superconductivity.

Therefore, our measurements of the spectrum of SnSe$_2$ on graphite in magnetic field are strong evidence that it is not superconducting. Other evidence for superconductivity in this system, such as the apparent vortex in Zhang et al. (2018), might be explained instead by the gap’s dependence on film-substrate interactions. Their measured gap was homogeneous within domains, only changing near or past a step edge in...
the underlying multilayer graphene.

A better explanation would be that band folding due to a Moiré pattern allows interaction between previously-independent electron states. This effect could be present even for the bilayer, albeit more weakly, and could allow inter-band interaction leading to an avoided crossing not spanning the Fermi energy. More complicated structure can also arise when the energy scales of the band folding and the inter-layer coupling are close to each other, as in the case of magic angle bilayer graphene [115]. In our measurements, the relationship between angle and gap size isn’t monotonic. This might be evidence that some other factor is affecting the gap size, or it might reflect this possibility of change in the density of states on a sub-1° angular scale.

We can’t rule out changes in chemical potential or band shape due to coupling between the substrate and the monolayer. One probe of this coupling is the relative height of the surface measured via STM. This information was extracted from scans containing multiple domains, taken at a bias of 300 mV. We measured differences in height on the scale of 10 picometers (see Tab. 4.1). The height can either change due to shift in the position of the nuclei themselves, or change in the local density of states. Because the height roughly decreases with increasing twist angle, rather than increasing as the heterostructure moves from its equilibrium position, it’s more likely that the height change is due to a change in density of states, mediated by twist angle. Given the work function of SnSe$_2$ [125], this change in the height of the surface of constant current could be caused by a change of approximately 10% in the local density of states, either due to a change in the band shape or due to a shift of the chemical potential by as little as 21 meV, although we don’t detect any shift in spectra with 10 mV resolution.

<table>
<thead>
<tr>
<th>Angle</th>
<th>Height</th>
<th>Gap Size</th>
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<tbody>
<tr>
<td>30°</td>
<td>10 pm</td>
<td>2.2 mV</td>
</tr>
<tr>
<td>31°</td>
<td>2 pm</td>
<td>3.3 mV</td>
</tr>
<tr>
<td>33°</td>
<td>8 pm</td>
<td>2.9 mV</td>
</tr>
<tr>
<td>35.5°</td>
<td>0 pm</td>
<td>1.6 mV</td>
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Table 4.1: Height order, angle order, and gap order of regions.

Overall, our scanning tunneling microscopy measurements of SnSe$_2$ monolayer on graphite, at low temperature and high magnetic field, rule out superconductivity despite replicating previous observations at zero magnetic field. We measure a difference in density of states between regions with different twist angle, and a gap centered at the Fermi energy that depends non-monotonically on the twist angle. This is indicative of Moiré pattern physics at work in this heterostructure, though more experimental and theoretical investigation is needed.
Chapter 5

FeSe

5.1 Introduction

5.1.1 Iron-based Superconductors

Iron-based superconductors were discovered in 2006 with the measurement of superconductivity at 4 °K in the layered oxy-pnictide (meaning it contains both oxygen and an element in the same column as nitrogen, such as phosphorous or arsenic) LaOFeP by Kamihara et al. [126], which was part of a deliberate search for unconventional superconductivity in compounds with some similarities to high-T_c cuprate superconductors. High-T_c superconductivity was soon found in the compound La(O_{1-x}F_x)FeAs by the same group [127], and T_c among bulk iron-based superconductors has been measured as high as 56 °K[128][129].

Iron-based superconductors in their normal state tend to be near the boundary of two different states: an antiferromagnetic spin-density-wave (SDW) state caused by magnetic interactions between electrons, and a non-magnetic metallic state sometimes distinguished as being a "bad metal." By this it is meant that iron-based superconductors even in the normal state have a renormalized (larger) electron mass due to correlations, high susceptibility to spin fluctuations, and strong orbital dependence of electron-electron interactions [130]. This is also sometimes called a "Hund’s metal" state, referencing Hund’s rule from chemistry or atomic physics that electrons prefer to be in different orbitals and have the same spin to minimize the Coulomb potential - this same sort of interaction leads to interesting behavior in multi-orbital tight binding models [131]. Iron-based superconductors’ Fermi surfaces tend to all be similar, being semimetallic with hole-like bands near the center of the Brillouin zone and electron-like bands at the M point [132]. However, some iron-based superconductors break this pattern, typically by having the same general band structure but a chemical potential that is above or below the area of overlap between the bands, as in hole-doped BaFe_2As_2 [133] or potassium-dosed FeSe [134].

Theoretical understanding of superconductivity in iron-based superconductors is fairly good on a qualitative level, but hasn’t found quantitative, predictive success. Iron-based superconductors are often thought
Figure 5.1: Schematic phase diagram of the iron pnictides / chalcogenides on hole or electron doping. The position of the nematic (i.e. spontaneous electronic symmetry breaking) phase transition relative to the SDW transition is subject to debate. The superconducting pockets at high doping are not intended to be universal, but reflect the behavior of KFe$_2$As$_2$ [135] and K$_x$Fe$_{2-y}$Se$_2$ [136]. Figure from Basov and Chubukov 2011 [137].

of in terms of Cooper pairs bound by exchange of spin fluctuations[132]. Spin fluctuation mediated pairing, unlike the phonon case, promotes pockets of opposite sign of the order parameter in momentum-space, connected by the wavevector of the local spin wave excitation. Although the plane-wave, weak coupling explanation for the magnetic interactions based on Fermi surface nesting is appealing [132][140], strong-coupling models such as the multi-orbital Hubbard model can produce the same qualitative band structure [141][142][131]. Additional data in favor of stronger coupling comes from the existence of highly doped iron-based superconductors (see Fig. 5.1) without straightforward Fermi surface nesting, and local moments measured by experiment [143]. However, calculations in the strong coupling regime are generally only tractable after some simplifying assumptions, such as reducing the number of orbitals considered, and depend on parameters whose effective values have to be learned empirically. We are still several breakthroughs away from having the necessary tools to calculate the low-energy electronic structure from first principles.

5.1.2 FeSe

Iron-selenium compounds form in many different ratios, including FeSe, FeSe$_2$, Fe$_3$Se$_4$, and Fe$_7$Se$_8$ [144]. Structures range from hexagonal layers to fully connected non-centrosymmetric lattices, but what we are
interested in here is what is sometimes labeled the $\beta$ phase of FeSe, the layered PbO-type structure with fourfold symmetry, first analyzed by Hagg and Kindstrom in 1933 [145]. Little attention was paid to this material prior to the discovery of iron-based superconductors, aside from its documentation in the iron-selenium phase diagram and a solitary paper on the growth of polycrystalline films containing it [146]. However, after 2006, it has naturally attracted focused interest as the chemically simplest iron-based superconductor.

Bulk FeSe crystals were found to have a superconducting $T_c$ of 7.8 °K [147] to 9 °K [148]. Measurements indicate at least some nodes in the superconducting gap, despite presumed overall $s^{\pm}$ symmetry [149][150]. The $T_c$ can be raised to 30 °K by pressure [151] or by intercalation with potassium [136]. The band structure in the bulk is, as with typical iron pnictides and chalcogenides, semimetallic, with quasi-2D hole and electron Fermi surface pockets. However, under pressure, strong electron doping, and growth on SrTiO$_3$, the band structure shifts and the Fermi surface no longer includes a hole-like pocket [152]. FeSe is on the electron-doped side of the phase diagram in Fig. 5.1, and undergoes a structural phase transition from tetragonal (square lattice) to orthorhombic (rhombic lattice) structure at 70 °K [153], accompanied by symmetry breaking in the electronic structure [154]. This broken symmetry is also reflected in the superconducting phase, which has anisotropic Ginzburg-Landau parameters as evidenced by the elliptical vortices [149][155] formed between the (perpendicular) critical magnetic fields $H_{c1}$=25 Oe [156] and $H_{c2}$=17 T [148]. In addition to DFT band structure calculations [5], there are also tight-binding predictions of the Fermi surface structure [157] (see Fig. fig:dftBands). ARPES measurements made also back up this anisotropic picture of the Fermi surface [158][159].
In 2012, Qing-Yang Wang et al. reported that their specific method of growing a single atomic layer of FeSe on the (001) surface of strontium titanate (SrTiO$_3$) can raise the $T_c$ to approximately 65 °K[161], which further work would push to around 100 °K[162]. This is despite $T_c$ of multilayer thin films of FeSe on STO dropping as films are made thinner[163]. As a single layer on STO, the Fermi surface is different than in the bulk, only consisting of the electron-like pockets at the edge of the Brillouin zone, and the superconducting gap is a nodeless s-wave gap [164]. The structural phase transition is suppressed by interaction with the tetragonal substrate, although there’s some uncertainty on whether the electronic state is natively and/or magnetically ordered [163][165][166][167][168]. Transmission electron microscopy work shows that the film-substrate interaction deforms both the film and the top TiO$_2$ layer of the substrate (of which the properly prepared substrate has a double layer at the surface), and that the transition of the film from non-superconducting to superconducting as it is annealed involves small changes in the selenium content of both the film and the substrate, as well as, surprisingly, a slight increase in distance between the film and substrate [169]. Charge transfer doping with donor atoms has also been shown to promote superconductivity in FeSe monolayers [170]. Another important factor of this system is the high-energy phonons due to motion of the oxygen atoms, which have been shown to penetrate into the FeSe film [171][172] and potentially promote superconductivity via the ordinary Eliashberg-type mechanism, in conjunction with
the terms more typical to iron-based superconductors.

Thin films of $\beta$-FeSe have been grown on other substrates, with varying results. On pure TiO$_2$, similar results obtain to STO [173]. When grown on graphene, which interacts relatively weakly with the FeSe film, band structure and $T_c$ were similar to bulk (8 $^\circ$K) in an 8 layer (5 nm) thick film, but $T_c$ was suppressed to 3.7 $^\circ$K as thickness was reduced to 2 layers [174]. Growth of thin films on the order of 100 nm in thickness, and therefore essentially bulk-like in band structure, has been done on a variety of substrates including on LaAlO$_3$, SrTiO$_3$, and MgO via pulsed laser deposition [175][176]. On some of the substrates, these films show a possible superconductivity enhancement over bulk, albeit with $T_c$ strongly decreasing as the film thickness is reduced to 20 nm. X-ray diffraction found no correlation between the substrate in-plane lattice constant and $T_c$ for 160 nm thick films grown on different substrates, but the films had differences in the c-axis lattice constant, with larger spacing between layers strongly correlated with higher $T_c$. As thickness was varied, however, strain and $T_c$ co-varied [176].
We wanted to grow and study this high-Tc FeSe monolayer to better understand what unique properties of this system promote its superconductivity. We have developed instruments and recipes to grow FeSe and Fe(Se,Te), but haven’t been able to grow monolayer films of sufficient quality to study superconductivity. Instead, we have to content ourselves with studying the electronic structure of the few-layer FeSe on STO, which, unlike the monolayer, actually has its superconductivity suppressed. We hope to elucidate the thickness effect suppressing superconductivity for thinner films.

### 5.2 Growth

The substrate used for growth was 0.7% niobium-doped STO(001) purchased from Shinkosha Co. The doping is necessary for STM, which requires a conducting electrical circuit between the sample and the tip. At 0.7% Nb doping, bare STO still has density of states too small to scan at low bias voltage with STM, but it is sufficiently conducting to carry charge away from islands of conducting FeSe.

STO in the 001 direction is made of alternating SrO and TiO$_2$ planes. Typical practice (e.g. Qing et al. 2012 [161]) is to prepare the substrate such that it terminates in a titanium oxide plane. Obtaining an atomically flat titanium oxide plane on the STO(001) substrate was actually the main challenge in growing high quality FeSe. The eventual best performing recipe was to begin with clean STO substrate, etch in 10M HCl for 40 minutes at room temperature, etch in 70°C water for 1 hour with ultrasonic cleaning, anneal at 1100°C for 2 hours under oxygen, and then in vacuum anneal at 500°C with selenium vapor for 3 hours. This preparation recipe has also been successfully used by labmates working with STO.

The logic behind this preparation procedure is that SrO is more easily dissolved in HCl and in hot water than TiO$_2$. This means that if the STO surface is rough, etching will preferentially extend horizontally at exposed SrO planes, flattening the surface and exposing TiO$_2$. Annealing under oxygen further flattens the surface, visible under AFM or STM as increasing the distance between step edges, and removes oxygen vacancy defects. Annealing in vacuum cleans the surface and removes any residual SrO, and there is some speculation in the literature about selenium substituting into the STO(001) surface or vacuum annealing promoting a particular surface reconstruction[177].

STM measurements on three samples are covered here, each with different growth conditions. For the thickest film (approximately 3 nm), the K-cell temperatures were 1150°C for Fe and 156°C for Se, corresponding to nominal fluxes (measured with QCM) of 0.11 and 1.2 Å/min. The substrate was heated to 370°C and deposition proceeded for 30 minutes, after which the film was annealed at 400°C for 2 hours.

For the 2- and 3-layer film, the K-cell temperatures were 1250°C for Fe and 170°C for Se, corresponding
to nominal fluxes of 0.89 and 2.9 Å/min. The substrate was heated to 370 °C, film was grown for 1 minute and 10 seconds, after which the film was annealed at 450 °C for 4 hours. The sample with monolayer FeSe was grown with Fe at 1200 °C, Se at 165 °C, nominal fluxes 0.24 and 2.3 Å/min, substrate at 350 °C. Growth time was 1 minute, followed by annealing for 3 hours at 380 °C.

5.3 STM Measurement

5.3.1 3 nm film

Figure 5.5: a: Topography of 3 nm FeSe film on STO, 400x400 nm, taken at a bias of 460 mV and current of 51 pA. b: Spectrum of 4 nm FeSe film.

The topography of the 3 nm FeSe film is very flat, with steps approximately every 200 nm. There are two finer details visible in Fig. 5.5. First is the quasi-periodic pattern of slightly raised regions in the film. This is likely due to the mismatch in lattice constants between the film (bulk lattice constant 3.76 Å) and the substrate (lattice constant 3.90 Å)[178]. The film can relax strain by periodically slipping with respect to the substrate, leading to a pattern of periodic buckling. This process becomes more favorable as film thickness increases.

The tunneling spectrum of the film closely matches the predicted bulk band structure (comparing Fig. 5.5b to Fig. 5.4a), with higher density of states in the several valence bands than in the conduction bands. However, the bulk band structure has quite sizeable semimetallic overlap between the opening of the conduction bands and the closing of the valence bands, while the spectra on the film go almost completely to zero, indicating that the bands have pulled apart by approximately 500 meV.

STM topographs of the FeSe surface reveal two main kinds of defects. The most obvious are the bright
dimers, which often are called "dumbbell defects" after their shape. These defects are iron-site vacancies (note that they are centered on the iron sites that are directly in between the top layer selenium atoms in FeSe). Even though they are vacancies, the local density of states at the surface increases due to Se orbitals being freed up from bonding. The less common defects in this film are selenium vacancies, which simply look like a missing atom in the selenium lattice. The predominance of iron vacancies in this film indicates that it is slightly selenium-rich relative to the ideal stoichiometric ratio, which can be improved by increased annealing time or temperature.

Figure 5.7: a: Highly detailed topography 86x86 nm, taken at a bias of 140 mV and current of 110 pA. b: Strain map of the central 78x78 nm region of image a. Red is stretched by up to 0.7% relative to blue. The compressed blue spots correspond to raised regions on the topography.
We measured the periodic strain of this thin film via the Lawler-Fujita algorithm described in an earlier chapter, which measures the displacement of atoms in an image from a perfect lattice. This required taking a large, high-resolution image with exogenous drift due to piezo hysteresis as low as reasonably achievable. The full strain tensor can then be calculated as the Jacobian of the displacement field, but what we typically care about is simply the trace of the strain tensor, which can be interpreted as the fractional change in area of a unit cell on the surface.

This process, as shown in Fig. 5.7, uncovers periodic strain, as expected. The slightly raised regions in the topography are slightly compressed relative to their surroundings. If we expect the film to be gridded by lines of slippage that insert an extra column of atoms relative to the underlying substrate, then maybe the raised regions are actually the intersection points of these lines. The periodicity of these regions is approximately 36 nm, which would be a 1.0% strain if an extra unit cell is inserted with that periodicity. This is comparable to the measured periodic strain variation of 0.7%, but not sufficient to compensate for the 3% difference in lattice constant between FeSe and SrTiO$_3$. We can conclude that the sample is still experiencing a net strain, the strain being only partially relaxed by the periodic buckling.

One notable feature of the FeSe surface is its division into long stripes, separated by domain walls. The conductance maps in Fig. 5.8 highlight these domains. These domains are the product of the structural phase transition from tetragonal (square lattice) to orthorhombic (rhombic lattice) that FeSe undergoes near 90 °K[179], which has two possible ways of breaking the rotational symmetry. This phase transition is thought to be driven by symmetry-breaking electron ordering at low temperatures [180].

In Fig. 5.8, we show two different conductance maps on the same area - the topography was scanned while also measuring the differential conductance via the lock-in method. After binning the maps by domain type, using a mask with edges smoothed by a gaussian to reduce high-frequency components, the Fourier transform of the bins shows the QPI in the two regions. As you can see, the QPI in the two regions shows clear symmetry breaking, with the two regions appearing to be related by a reflection across a diagonal line through the Bragg points. The measured lattice vectors also change slightly, shifting by 1.8° relative to each other between the two regions.

These two QPI patterns actually differ in terms of consonance with theoretical prediction. Our expected QPI, based off of the tight-binding prediction of the bulk Fermi surface, can be seen in Fig. 5.11. This predicted QPI is made by first separating the Fermi surface into separate orbital components, then assuming a uniform scattering matrix within the first Brillouin zone and calculating the predicted scattering for the three orbitals, then re-combining them. First, compare the predicted QPI for negative bias with our negative-bias data, which is the lower row in Fig. 5.8. The agreement with prediction shows the existence of two
Figure 5.8: Selected images and Fourier transforms (FT) showing QPI in FeSe. **Left:** Topography of the 68x68 nm region where the conductance maps were taken, scanned at 140 mV. Note that the field of view can be separated into two differently oriented types of domain, which at 140 mV can be distinguished by different electron densities. **Top row:** 560x560 pixel conductance map taken at +80 mV, current 18 pA. Due to finer resolution in real space, the Fourier transforms in the top row extend beyond the first Brillouin zone. **Bottom row:** 368x368 pixel conductance map taken at -80 mV, current 45 pA. Before taking the Fourier transforms, the map was spatially split according to domain. "Larger region" refers to the portion of the image that is darker in the topography and first conductance map, while "smaller region" refers to the brighter. Fourier transforms were two-fold symmetrized.

Fermi surface pockets - there is inter-pocket QPI at vector $q_2$, not just the intra-pocket QPI at the center and around the Bragg peaks. Conductance maps at -100 mV and -40 mV show similar patterns, but with different sizes of the central ring suggesting that a hole-like circular Fermi surface pocket is closing at close to -20 meV (and naturally, removing one of the bands removes the inter-band scattering).

An important feature of the predicted QPI is that both the base model from Kostin et al.[160] and our QPI processing treat the effective unit cell as containing only one iron atom. This is a phenomenon called Brillouin zone unfolding [181], which has been seen previously in iron-based superconductors. In the normal unit cell of FeSe there are two iron atoms related by a glide-reflection symmetry but not translational symmetry. But if we calculated QPI using this unit cell (and its corresponding Brillouin zone), the electronic anisotropy would by almost totally suppressed due to umklapp scattering. However, if the electrons for some reason see a unit cell only one iron atom in size, then the Brillouin zone "unfolds" by a factor of $\sqrt{2}$, the pockets that were previously at the corners become inequivalent, and our predictions closely match the data.

The upper row in Fig. 5.8 is harder to interpret. Due to higher resolution in this map, we can better
Figure 5.9: Predicted orbital-preserving QPI for a single domain based on the model from Kostin et al. 2018 [160]. QPI prediction was done by summing separate autocorrelations of the different orbital components of the Fermi surface. 

- **a**: Predicted bulk Fermi surface with main scattering vectors shown. Multiple pockets are connected by vector $q_2$.
- **b**: Predicted negative-bias QPI, directly from Fermi surface in a.
- **c**: Predicted positive-bias QPI, with no central hole pocket and larger electron pockets.

Resolve the scattering between pockets in neighboring Brillouin zones, showing broken rotational symmetry that may point to the bands having unusual orbital texture. Explaining the alternating-chirality "pinwheel" shapes of the QPI near the Bragg peaks in terms of solely inter-pocket QPI requires an unusual band structure, because all the Bragg peaks are connecting the same pairs of pockets, up to rotational symmetry. See Fig. 5.10 for an example of scattering between opposite-chirality pockets that would suffice to explain the QPI observed. Another unusual feature of the positive-bias QPI is that there is also QPI that is extended through q-space, not just clustered near the center and the Bragg peaks. Although in the larger region this looks like inter-band scattering between quasi-1D bands, another interpretation is that this is intra-band scattering in a pocket with radius very close to 1/2 the reciprocal lattice spacing, which has a preferential scattering direction due to the electronic ordering. To remain compatible with the observed scattering at small q-vector, this large pocket would likely be concentric with a smaller Fermi surface pocket. Maps at 110 mV and 170 mV bear out this interpretation somewhat and also show the QPI pattern becoming more elliptical rather than circular. However, neither explanation is fully consonant with the theoretically understood band structure, and we don’t have QPI data near the Fermi energy to directly show us the origin of the extended part of the QPI pattern.

Looking at the intra-pocket QPI rather than the inter-pocket QPI, we can see broad agreement with the theoretical picture, specifically providing evidence for the "dog-bone" shape of the electron-like pocket, and the fact that the middle and ends of the dog-bone have different orbital character (see Fig. 5.12). Previous QPI measurement on normal-phase FeSe is found in Hanaguri et al. 2018 [182], which measured only the intrapocket QPI. Although our data has slightly lower resolution in k-space and covers a different energy
range (their data comes from a set of conductance spectra within 25 meV of the Fermi energy), our data lead to equivalent conclusions about the shape and orbital character of the Fermi Surface.

There is one more striking detail of the top conductance map in Fig. 5.8, which is that the different domains have different local density of states. At higher energies (170 mV) the effect is reversed, indicating that the electron DOS is concentrated at different energies in the two domains. We can only offer some possible explanations of this phenomenon. The most exciting is that this is due to the interplay between strain and nematicity - looking at the strain patterns in the two different regions, they appear to be systematically inequivalent, with one region containing an alternating pattern of compressive and tensile strain while the other has a more uniform compression (albeit with variation in strain direction). Other explanations could be that the electronic state spontaneously breaks vertical symmetry, that there is some subtle and unusual momentum-dependent tip effect despite the high image quality, or that the entire region is under net uniaxial strain in a way that differentially affects the band structure of the two different orthorhombic domains. More study of periodically strained FeSe could help uncover the answer.

**5.3.2 3 layer film**

Growing a thinner film did not simply result in a continuous reduction in height. At 2-3 layers of FeSe, the film transitioned to growth in islands, and reduced deposition of material in other attempts reduced the size
Figure 5.11: Predicted orbital-preserving QPI for a single domain based on the model from Kostin et al. 2018 [160]. QPI prediction was done by summing separate autocorrelations of the different orbital components of the Fermi surface. a: Predicted bulk Fermi surface with main scattering vectors shown. b: Predicted negative-bias QPI, directly from Fermi surface in a. c: Predicted positive-bias QPI, with no central hole pocket and larger electron pockets.

5.3.3 Monolayer film

Using the latest substrate preparation procedure along with somewhat lower substrate temperature, reduced deposition of material did result in the growth of regions of monolayer FeSe. These islands were still small and had a high defect concentration. These monolayers were strongly insulating, with a bandgap of greater than 1 eV. This completes the pattern seen above that for thinner FeSe films, the valence and conduction bands are forced apart relative to the bulk.

Improving the growth quality would likely require further refinement of substrate preparation processes and growth conditions. Higher growth and annealing temperatures would help reduce defect concentration and avoid the growth (visible in Fig. 5.14 of other iron-selenium compounds. One method of improving
substrate preparation is to improve the sample holder used, to allow for higher temperature vacuum annealing using e-beam heating. This improvement has been implemented with partial success, and was used for substrate preparation when growing Fe(Se$_x$Te$_{1-x}$).
Figure 5.13: a: Topography of 2- and 3-layer FeSe on STO, 300x300 nm, taken at a bias of 1 V and current of 130 pA. b: Spectrum of 3-layer FeSe.

Figure 5.14: a: Topography of monolayer FeSe on STO, 20x20 nm, taken at a bias of -2.5 V and current of 30 pA. b: Spectrum of monolayer FeSe.
Chapter 6

Fe(Se\textsubscript{x}Te\textsubscript{1-x})

6.1 Introduction

FeTe, relative to the electron-doped FeSe, is in the center of the iron-based superconductor phase diagram from Fig. ?? It is not a superconductor but undergoes a magnetic and structural phase transition at 70 °K to an antiferromagnetic, monoclinic phase [183]. This parent compound can become superconducting upon alloying with the other chalcogenides sulfur [184] or selenium [185][186], or by other methods such as strain [187][188] or excess iron [189], all of which tend to simultaneously suppress the antiferromagnetic order. We actually see similar levels of strain as Ciechan et al. 2013 [188], but biaxial and periodic rather than uniaxial, which changes the effect on the magnetic and superconducting states. Alloying also tends to suppress the structural phase transition, by a combination of disorder and weakening the associated magnetic phase. For Fe(Se\textsubscript{x}Te\textsubscript{1-x}), the symmetrical tetragonal phase persists to low temperature between \(x = 0.45\) and \(x = 0.8\); closer to FeSe the crystal tends to transition to the orthorhombic phase, closer to FeTe and it transitions to the monoclinic antiferromagnetic phase.

![Figure 6.1: Phase diagram of Fe(Se\textsubscript{x}Te\textsubscript{1-x}) from Dong et al. 2011 [186].](image)

Thin films of Fe(Se\textsubscript{0.5}Te\textsubscript{0.5}) have been grown via pulsed laser deposition on various substrates, including
including LaAlO$_3$, CaF$_2$, SrTiO$_3$, and MgO [190]. $T_c$ of these films negatively correlates with the in-plane lattice constant of the substrate. Bellingeri et al. attribute this to a dependence on tetrahedral bond angle, with a preferred angle of 109 degrees [190]. Hanaguri et al. 2010 did STM study of bulk crystals of Fe(Se$_{0.5}$Te$_{0.5}$), which after oxygen annealing to remove excess iron showed evidence of s± superconducting symmetry [191]. This was determined by measuring the quasiparticle interference pattern as a function of magnetic field, which differentially affects sign-preserving and sign-reversing scattering processes. Chen et al. grew monolayers of Fe(Se$_x$Te$_{1-x}$) on STO and studied them using STM. They saw a $T_c$ enhancement, inferred a sign-reversing pairing symmetry from scattering near magnetic impurities [192], and see unusual bound states on line defects that they attribute to Majorana fermions [193], which leads us into the discussion of topological states.

Fe(Se$_x$Te$_{1-x}$) has nontrivial topological character. Wang et al. 2015 [194] used DFT calculations to show that FeSe and Fe(Se$_{0.5}$Te$_{0.5}$) have a relative band inversion, with bands with large component from the $p_z$ of the chalcogen atoms crossing with other bands. This is due to Te content enhancing interlayer hopping. Fe(Se$_{0.5}$Te$_{0.5}$) was shown to have the nontrivial topological invariant, and a topological surface state was predicted with a Dirac cone (i.e. a conical part of the dispersion relation with zero effective mass) near the Fermi energy and a peak in the DOS at approximately 60 meV. They then also used ARPES in combination with surface doping to show that there did appear to be states with the predicted dispersion relation [194]. This discovery started the search for topological superconductivity, i.e. a superconducting gapping of the spin quantum Hall state, in Fe(Se$_x$Te$_{1-x}$) [195][196]. Gapping out the surface state requires a helical p-wave superconducting state, and is expected to host unusual Majorana excitations[197][198], and is also of interest because it fulfills the requirements to implement topological quantum computation [199]. Some STM studies at low temperature ($T<0.1\,\text{K}$) show showed zero-bias peaks in the DOS inside vortex cores under weak applied magnetic field [200][201], which are associated with Majorana excitations on the end of the 1D normal-state wire formed by the vortex as in Kitaev 2001 [197]. This is evidence of only medium strength because of the existence of alternate methods for in-gap states such as Caroli-de Gennes-Matricon states [202], which can resemble a zero-bias peak in realistic materials [203]. The most conclusive evidence came from further ARPES study, which showed using spin-resolved and low temperature ARPES that the states found in [194] indeed had helical spin texture, and that below the $T_c$ of the bulk they started to develop a radially symmetric quasiparticle peak [204].
6.2 Growth

Fe(Se,Te) films were grown on either highly oriented pyrolytic graphite (HOPG), or on niobium-doped strontium titanate (STO). Preparation of HOPG is simple - it is mounted to the sample holder with a high temperature silicate adhesive made conductive by carbon particles, and then it can be cleaved in air and still have a pristine surface after degassing in vacuum. Cleaving can be done with silicone adhesive tape, chosen because the silicone adhesive leaves negligible residue even when it touches the metal parts of the sample holder.

The preparation of STO substrates is more involved. We use 0.7% Nb doped SrTiO$_3$ (001) (abbreviated STO) substrates from Shinkosha Co. The niobium doping ensures conductivity of the substrate sufficient for STM measurement. Similar to previous publications[205][206], we use aqueous etching to preferentially etch the strontium oxide plane and expose a titanium oxide surface. We use 60 minutes submersion in 10 M hydrochloric acid at room temperature, followed by 60 minutes in 70$^\circ$C H$_2$O with occasional agitation.

After etching, the substrates are annealed. These annealing steps make the atomically flat terraces of the substrate flatter and more uniform, as well as encouraging the surface to find a stable surface reconstruction. In our quartz tube furnace, the substrates are kept under an oxygen atmosphere annealed at over 1000$^\circ$C for at least 2 hours. Our tube furnace measures temperature using a thermocouple that is close to the heating element, and so setting the nominal temperature for 1100$^\circ$C is necessary to pass 1000$^\circ$C at the substrate location. After annealing under oxygen, the substrates are then clamped to the sample holder and transferred into the MBE, where they are annealed in vacuum for 1 hour, effectively under slow selenium (Se) flux due to the high vapor pressure of Se. This vacuum annealing step is done using e-beam heating of the substrate, and is limited to up to 800$^\circ$C for our sample holder design due to the risk of the substrate cracking from thermal expansion differential between the center and the edges.

Growth takes place in our home-built mini-MBE, which is described in Chapter 2. Iron (Fe) flux is the limiting reagent in the film growth, and is kept at approximately 0.5 Å/minute. Selenium being more reactive with iron than tellurium, the selenium flux is set close to its stoichiometric value. The number density (atoms per volume) of iron is 2.3 times greater than the number density of selenium, and so for Fe(Se$_{0.5}$Te$_{0.5}$) growth the stoichiometric value would be 0.58 Å/min. However, this doesn’t take into account the vapor pressure of the selenium deposited on the walls of the chamber. This is only approximately 10$^{-10}$ Torr at room temperature, but rises exponentially if the chamber walls are warmed due to radiant heat from the K-cells and sample holder. Recalling that 1 Langmuir (approximately 2.9 Å of material) is 10$^{-6}$ Torr over 1 second, if the Se vapor pressure is approximately 10$^{-9}$ Torr, this is an effective deposition rate of approximately 0.2 Å/min. These considerations only matter if tellurium (Te) is also being deposited - if it is not, then the
selenium can be deposited in excess. When Te is included, it is what can be used in excess, which in practice means at a rate (in Å/min) 5 to 10 times greater than the rate of iron deposition.

The film is grown with the substrate heated via radiative heating, with temperature circa 300°C for Fe(Se<sub>x</sub>Te<sub>1−x</sub>), compared to over 400°C for just FeSe. The lower temperature makes it easier to control the Te/Se ratio because lower temperature reduces the impact of FeSe’s greater stability relative to FeTe during growth. However, it’s likely that further exploration of growth and annealing recipes would allow for the usage of higher temperatures to reduce the concentration of structural defects. See Table 6.1 for a list of conditions for the films grown on STO referenced in this chapter. Values for source temperatures are the PID controller setting, elemental fluxes are measured by prior calibration with QCM, substrate temperature is from calibration both via thermocouple thermally bonded to a substrate and pyrometer reading, layer number is estimated from iron deposition and phenomenological RBS data (see below), and composition is measured from STM topography.

<table>
<thead>
<tr>
<th>Fe temp (°C)/ rate (Å/min)</th>
<th>Se °C/ Å/min</th>
<th>Te °C/ Å/min</th>
<th>grow time (min)/ max temp (°C)</th>
<th>layers</th>
<th>Te %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1250°/0.44</td>
<td>136.5°/0.19</td>
<td>282°/3.5</td>
<td>16/280°</td>
<td>15.1</td>
<td>81%</td>
</tr>
<tr>
<td>1250°/0.44</td>
<td>138.5°/0.24</td>
<td>282°/3.5</td>
<td>10/285°</td>
<td>9.4</td>
<td>21%</td>
</tr>
<tr>
<td>1250°/0.44</td>
<td>144°/0.40</td>
<td>282°/3.5</td>
<td>8/280°</td>
<td>7.5</td>
<td>38%</td>
</tr>
<tr>
<td>1250°/0.3</td>
<td>136°/0.23</td>
<td>265°/0.9</td>
<td>12/280°</td>
<td>7.7</td>
<td>49%</td>
</tr>
<tr>
<td>1250°/0.3</td>
<td>136°/0.23</td>
<td>265°/0.9</td>
<td>104/285°</td>
<td>66.8</td>
<td>25%</td>
</tr>
</tbody>
</table>

Table 6.1: Growth conditions, expected thickness, and measured compositions of several Fe(Se<sub>x</sub>Te<sub>1−x</sub>) thin films.

Figure 6.2: Results of Rutherford backscattering spectroscopy on Fe(Se<sub>x</sub>Te<sub>1−x</sub>) thin film on graphite, with theoretical fits and thickness estimate from SimNRA software.
The composition and thickness of some films grown on graphite were checked via Rutherford backscattering spectrometry (RBS). Growing on graphite is useful for RBS due to carbon’s low atomic mass eliminating overlap between the scattering peaks of the film and the substrate. The strontium in STO is unfortunately close in mass to selenium, making STO a poor choice for RBS substrate for selenides. Aside from validating that we did grow Fe(Se,Te), RBS data can be used to roughly estimate the thickness of films, due to the high sticking coefficient of iron. The film in Fig. 6.2 had over 76% of the nominal iron flux accounted for by the RBS fit to the film thickness. Treating this as a phenomenological parameter, we can estimate film thickness as 1 layer of Fe(Se\textsubscript{x}Te\textsubscript{1−x}) per 0.467 Å of nominal iron deposition.

### 6.3 Morphology and Film Quality

The film morphology was flat enough for STM study with many flat regions of over 50x50 nm on all films, but had a fairly high concentration of screw defects, as can be seen in Fig. 6.3. The average distance between step edges was 40-90 nm, depending on the sample and scan area. Film thickness and composition did not seem to greatly affect flatness.

![Figure 6.3: Representative large-scale morphology of Fe(Se\textsubscript{x}Te\textsubscript{1−x}) films. a: 81% / 15 layers. b: 49% / 8 layers.](image)

Concentration of Te versus Se was measured via STM topography (Fig. 6.4). Controlling film composition remained challenging throughout different experiments with thin film growth recipes. The ratio between the nominal Se flux as a fraction of Fe flux, and the fraction of Se incorporated into the film, varied between 0.5 (for the 81% Te film) and 2.3 (for the 21%, 25%, and 38% Te films). Moreover, the 49% and 25% Te films were grown with identical recipes, just with different thicknesses.
Part of this is due to the the selenium vapor pressure within the MBE, which can vary exponentially with the temperature of selenium-coated surfaces. This is especially important as annealing was carried out in the same chamber as growth. Future attempts to grow alloyed materials will have better control over post-growth and annealing procedures to try to control for this, moving to another chamber entirely when possible. However, this cannot be the whole explanation, again referencing the 49% and 25% Te films grown with the same recipe. One unverifiable possibility is that even with the same nominal Se and Te flux, the size and reactivity of the small chalcogen molecules emitted may have differed between growths due to differences in heat distribution in the K-cell. Another possible explanation based on growth kinetics is that Te should be favored at lower film thicknesses, both due to higher sticking coefficient to the STO substrate due to higher polarizability, and smaller lattice constant mismatch of FeTe compared to FeSe.

Figure 6.4: Atomic resolution topographies of increasing Te content. a: 21% Te, 10x10 nm. b: 25% Te, 9x9 nm. c: 38% Te, 10x10 nm. d: 49% Te, 10x10 nm. e: 81% Te, 10x10 nm.

The primary defect (Fig. 6.5, also visible in Fig. 6.4b and d) is centered at the Se/Te sites of the lattice, and seems to be more common within regions of Te atoms (the distribution of atoms in Fe(Se$_x$Te$_{1-x}$) being clustered rather than uniformly random). We’ll accord with previous work (e.g. Tamai et al. 2010 [207]) and attribute these to substitutions for iron atoms. Iron substitutions are expected to be magnetic[208], and therefore films intended to study superconductivity should be grown with a higher tellurium flux ratio to attempt to reduce this type of defect. There are also rarer examples of iron vacancies (defects centered on the iron site of the lattice) and adatoms or interstitial atoms located centrally between four Se/Te sites.

Measuring the lattice constant directly via STM is error-prone due to calibration drift, thermal effects, and piezo hysteresis. That said, we measure a nominal lattice constant of 3.96 Å for the 49% Te film and 3.955 Å for the 25% Te film, compared to measuring a bulk lattice constant of 3.935 Å with the same STM several months prior. Taken at face value, this implies that the films have a net strain of only 0.5-0.6%. This is much less than the 2 or 3% lattice mismatch expected for FeTe or FeSe, respectively, which would require the films to be relaxing their strain very quickly in the first several layers. However, similar to FeSe, these films still seem to show a pattern of brighter and darker regions on a similar length scale (faintly visible in
Figure 6.5: STM topography of region with defects on 81% Te film at the bias of maximum contrast. Bias -50 mV, current 50 pA.

Fig. 6.3, but more clear in Figs. 6.11a or 6.14a), which we associate with line defects relieving strain at the film-substrate interface.

### 6.4 Electronic Structure

![Figure 6.6: DFT band structure of FeSe (a) and FeTe (b) with orbital character shown. From Tamai et al. 2010[207].](image)

The predicted band structure is broadly similar to that of FeSe (see previous chapter)[5], with hole-like bands at the center of the Brillouin zone and electron-like bands at the center of the edge. However, we expect different orbital character of the bands as a function of % Te, with different compositions interpolating
between FeSe and FeTe [207]. Midway through this crossing, we expect Fe(Se\textsubscript{0.5}Te\textsubscript{0.5}) to have a band inversion that gives it nontrivial topological character [194].

Figure 6.7: Tunneling spectra on the scale of 0.25 V on thin films ranging from 0% to 81% tellurium content. Growth conditions are as in Table 6.1, except for a, which is the FeSe sample from the previous chapter. The rough trend is that increased tellurium content increases the density of states in the conduction band relative to the valence band, and also affects the indirect bandgap, making it more negative.

We measured tunneling spectrum across different film compositions (Fig. 6.7). The density of states was semimetallic, dropping nearly to zero at the Fermi level across a broad range of compositions, but the overlap between valence and conduction bands on average increased with increasing Te content. There may also be effects due to thickness, although comparing spectra across film thicknesses with similar compositions (Fig. 6.8) shows a somewhat ambiguous thickness effect of altering the relative DOS in valence and conduction bands without significantly opening or closing a gap.

Figure 6.8: a: Tunneling spectrum of 9.4 layer thick film with 21% Te content. b: Spectrum of 66.8 layer film with 25% Te content. Because of the scale degree of freedom, these spectra only convey the relative-magnitude information that in the thicker film, the DOS of the valence bands are greater relative to the conduction bands than in the thinner film.
We used quasi-particle interference measurement (QPI) to investigate the band structure of the 49% Te film. We detect inter-band scattering from -5 meV all the way up to 50 meV, a much broader range of band overlap than you would expect from the tunneling spectrum in Fig. 6.7 alone.

Figure 6.9: a: Topography of 50x50 nm region, bias -15 mV, current 50 pA. b: Conductance map of the same region at bias -5 mV, current 30 pA. Map has been masked to remove defect and noise associated with tip change.

Figure 6.10: Fourier transforms of conductance maps showing QPI on the 49% Te thin film. a: -35 mV, showing no inter-band scattering. b: at -5 mV there are the first signs of inter-band scattering at the expected points. c: The inter-band QPI signature is strongest near 5-10 mV. d: The inter-band QPI decreases slowly up to 50 mV, but some additional scattering is visible near the Bragg points.
6.5 Strain

We measured the spatially inhomogeneous strain of these films by taking high resolution topographs and applying the Fourier transform method for displacement field estimation outlined in the chapter on STM. You can see a comparison of strain in thinner and thicker films in Figs. 6.11 and 6.12. The most extreme features on the strain maps, the red/blue dipoles, are defects where one row of atoms abruptly terminates. On the side with more rows of atoms the lattice is under compressive strain, while on the side with fewer rows of atoms the lattice is under tensile strain. What we are mainly concerned with is not these defects, but the strain in the defect-free regions. The thinner film clearly has more long length-scale correlations in its strain, but both films have inhomogeneous strain on the 5 nm length scale. Some of this may be due to defects both in the top layer and the layers below, but most of this is due to inhomogeneity in composition of the film. The lattice constants of FeSe and FeTe differ by approximately 1%, and so Fe(Se$_x$Te$_{1-x}$) has unavoidable strain due to the inhomogeneous distribution of Se and Te. It is therefore only larger scale patterns as in Fig. 6.11 that we consider to be due to forces between the substrate and film.

![Figure 6.11: Topography (a) and associated strain map (b).](image)

We attempted to check the effect of strain on density of states, however, results were inconclusive. Spectra were taken along the linecut shown in Fig. 6.11, on the 49% Te thin film, and comparing the average spectrum in the positive versus negative strain regions finds that the DOS near the Fermi energy to be lower in the
regions of tensile strain, giving us Fig. 6.13a. On the other hand, on the 25% Te thicker film, spectra were taken near the pair of line defects in Fig. 6.12 that exogenously induce a region of high compressive strain. When comparing the region of compressive strain to the surrounding regions, we get Fig. 6.13b, where it’s the compressed region that has lower DOS near the Fermi energy. Finally, if we take a conductance map taken on a region of the 21% Te film that clearly shows the height modulation that we expect to correlate with strain (but where the strain was not measured due to the tip not having sufficient resolution), and compare the spectra in regions of different height, resulting in Fig. 6.14, we find no difference at all near the Fermi energy.

I think the most likely explanation of these conflicting results is that if there is a direct effect of local strain on spectra, it is smaller than as depicted in Fig. 6.13, which has to be explained by other factors. The spectra Fig. 6.13a might be selected not only for exogenous strain, but also for the strain due to Se/Te concentration, which could change the band structure. Fig. 6.13b might be due to the defect itself, not the induced strain.

### 6.6 Screw Dislocations

The density of screw dislocations on these films, together with the expectation that Fe(Se_{0.5}Te_{0.5}) should be topologically nontrivial, led us to study the density of states near the screw dislocations. In a topological insulator, we expect screw dislocations, and their associated line defects penetrating through the film, to host states, which are directly analogous to the edge states in the limit of weak coupling between layers of
Figure 6.13: Averaged spectra in regions of different strain. **a:** Averaged spectra from the linecut in Fig. 6.11. **b:** Averaged spectra in the dark blue (compressed) region of Fig. 6.12 compared to the surroundings. Error bars are standard deviation of the mean of the spectra.

Figure 6.14: **a:** Topography of region of 21% Te thin film, showing height modulations. **b:** Averaged spectra of the high regions (labeled "Compressive" based on expectation) compared to the low regions (labeled "Tensile").

the material [209][210]. These states have already been used to study other topological materials, such as bismuth [211].
Figure 6.15: Images on screw dislocations. a: Larger-scale topography from region with many screw dislocations. b through e: Topographies directly over four different screw dislocations, at bias voltage of 30 mV and current of 60 pA. f through i: Conductance map layers from maps in the scan region directly above. Each layer shown measures the LDOS at 16 mV bias voltage.

We took conductance maps on several different screw dislocations in two regions of the 49% Te film, the second region being shown in Fig. 6.15a. Finding localized states was difficult not because of a lack of features in the conductance maps, but because of too many - the inhomogeneity of the film is reflected in differences in spectra between different parts of the map, with correlation lengthscale approximately 1.5 nm. To avoid cherry-picking the data even accidentally, we checked for excess density of states at the screw dislocation by averaging all spectra within 1 nm of the center of the screw dislocation, determined by its position in the topography, and compared this to the average of all other spectra in the image.

Three of the four show excess density of states between 11 and 18 meV (Fig. 6.16). Unblinding ourselves and looking at the conductance maps in Fig. 6.15f through i, it’s plausible that there’s some state concentrated on the top step of the step edge (rather than centered on the center of the screw dislocation) and that this is present in the fourth conductance map as well, but was missed or drowned out by noise. Comparing this to the QPI data showing band overlap between -5 meV and at least 50 meV, this is potentially a signature of an edge state connecting these bands. Comparing this to the surface state DOS calculated by Wang et al. [194], this is the right energy to correspond to a Van-Hove singularity that would explain the peak.

One conductance map was also taken on a screw dislocation on the 81% Te film, and it’s plausible that a similar feature appears around 13 meV, but without several other screw dislocations to compare this to it’s difficult to draw firm conclusions.
Figure 6.16: a through d: Conductance map data from the maps corresponding to b through e and f through i in Fig. 6.15. The data has been binned by proximity to the screw dislocation - all points within 1 nm of the center of the screw dislocation are averaged as "Center," all other points are averaged as "Background." Error estimates of Center are the standard deviation of the mean with correlation length of the resolution of the tip, while error estimates of Background are the standard deviation of the mean but estimating the correlation length as 1.5 nm based on the correlation of the data.


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