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A Materials Study Of Topological Insulators And Two-Dimensional Ferromagnets

Sarah Friedensen
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A Materials Study Of Topological Insulators And Two-Dimensional Ferromagnets

Abstract
Topological insulators and two-dimensional ferromagnetic materials are novel phases with wideranging applications including quantum computing, spintronics, and other advanced electronic devices with the potential for ultrathin and ultralow-power wearables. TEM, AFM, EDS, Ramanspectroscopy, and low-temperature transport measurement are used to characterize an unusual superconducting alloy formed between palladium and bismuth selenide under low-temperature annealing. TEM, AFM, and EDS are used to perform a materials study of metallic nickel and niobium annealed with Bi2Se3 under similar conditions, with the conclusion that Ni reacts to form a diffuse layer within Bi2Se3 flakes that travels along edges and line defects, and Nb does not react at all. Detailed materials analysis of Bi2Se3 flakes nanosculpted with a gallium focused ion beam and with a TEM beam is also presented, with the result that FIB ablation causes the formation of a debris field alongside the edges of a cut region, but electron-beam ablation does not. Finally, a materials, defect, and degradation study of electrochemically exfoliated ultrathin vanadium selenide nanoflakes is presented, in which the VSe2 is characterized by Raman spectroscopy and a newly-invented MFM technique incorporating torsional resonance oscillation, as well as time studies of AFM, MFM, and low-temperature TEM to investigate the effects of both air and electrolyte exposure. It is found that propylene carbonate exposure causes the breakdown of VSe2 into its elemental constituents and that passivation with dilute perfluorodecane thiol confers a concentration-dependent protective effect. This research lays the groundwork for exciting future studies into the nature and properties of Group X alloys of Bi2Se3 and potentially novel spin textures and transport characteristics of VSe2 heterostructures.

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A MATERIALS STUDY OF TOPOLOGICAL INSULATORS AND TWO-DIMENSIONAL FERROMAGNETS
Sarah Friedensen
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in Physics and Astronomy
Presented to the Faculties of the University of Pennsylvania
in
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A MATERIALS STUDY OF TOPOLOGICAL INSULATORS AND TWO-DIMENSIONAL FERROMAGNETS

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Sarah Elizabeth Friedensen

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Dedicated to my father, who is every day a blessing.
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ABSTRACT

A MATERIALS STUDY OF TOPOLOGICAL INSULATORS AND TWO-DIMENSIONAL FERROMAGNETS

Sarah Friedensen
Marija Drndić

Topological insulators and two-dimensional ferromagnetic materials are novel phases with wide-ranging applications including quantum computing, spintronics, and other advanced electronic devices with the potential for ultrathin and ultralow-power wearables. TEM, AFM, EDS, Raman spectroscopy, and low-temperature transport measurement are used to characterize an unusual superconducting alloy formed between palladium and bismuth selenide under low-temperature annealing. TEM, AFM, and EDS are used to perform a materials study of metallic nickel and niobium annealed with Bi₂Se₃ under similar conditions, with the conclusion that Ni reacts to form a diffuse layer within Bi₂Se₃ flakes that travels along edges and line defects, and Nb does not react at all. Detailed materials analysis of Bi₂Se₃ flakes nanosculpted with a gallium focused ion beam and with a TEM beam is also presented, with the result that FIB ablation causes the formation of a debris field alongside the edges of a cut region, but electron-beam ablation does not. Finally, a materials, defect, and degradation study of electrochemically exfoliated ultrathin vanadium selenide nanoflakes is presented, in which the VSe₂ is characterized by Raman spectroscopy and a newly-invented MFM technique incorporating torsional resonance oscillation, as well as time studies of AFM, MFM, and low-temperature TEM to investigate the effects of both air and electrolyte exposure. It is found that propylene carbonate exposure causes the breakdown of VSe₂ into its elemental constituents and that passivation with dilute perfluorodecane thiol confers a concentration-dependent protective effect. This research lays the groundwork for exciting future studies into the nature and properties of Group X alloys of Bi₂Se₃ and potentially novel spin textures and transport characteristics of VSe₂ heterostructures.
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FIGURE 3.29: Elemental EDS maps of the annealed Bi$_2$Se$_3$ flake shown in Fig. 3.28(e) and atomic ratios across the cross-section of the flake. (a) Counts-per-second image of the annealed flake. (b) EDS map of the bismuth M$_\alpha$ line. (c) EDS map of the selenium L$_\alpha$ line. (d) EDS map of the palladium L$_\alpha$ line. (e) Atomic ratios of Bi:Se (red), Pd:Bi (blue), Pd:Se (green) across the cross section of the flake, starting with position 1 in the lower left-hand corner of the inset, and ending with position 6 in the upper right-hand corner of the inset.

FIGURE 3.30: Diffraction analysis of Bi$_2$Se$_3$ flake. (a) TEM image of the PdBi$_2$Se$_3$ flake analyzed. (b) SAED pattern at circle 1 in (a). (c) SAED pattern at circle 2 in (a), showing the presence of many different crystals and orientations. (d) SAED pattern at circle 3 in (a), also showing many different crystals and orientations.

FIGURE 3.31: SAED analysis of a considerably thinner flake on the same window as the flake analyzed in Fig. 3.30. In (a), the red circles on the phase-contrast image indicate regions used for collecting diffraction patterns. (b) Diffraction pattern from region 1 in (a), far from the Pd lead. (c) Diffraction pattern from region 2 in (a), on top of the region where the Pd lead was absorbed. (d) Diffraction pattern of region 3 in (a), atop the Pd lead far from the Bi$_2$Se$_3$ flake.
FIGURE 3.32: Raman spectroscopy of Pd-alloyed exfoliated Bi$_2$Se$_3$ flakes on SiO$_2$. (a) Optical images of the Bi$_2$Se$_3$ flake (light gray) with an absorbed 90 nm Pd strip in the middle (dark gray). The bright spot in each image indicates the position of the Raman laser. Position 1 is far from the Pd strip; Position 2 is atop the Pd strip; Position 3 is to the left of the Pd strip; and Position 4 is to the immediate right of the Pd strip. (b) Raman scattering spectra of positions 1 to 4 within the range of Bi$_2$Se$_3$ phonon peaks. Spectra from positions 1, 3 and 4 show peaks that agree with measurements of pure Bi$_2$Se$_3$. The spectrum for Position 2 has no peaks because the Pd layer atop the Bi$_2$Se$_3$ is opaque to 514 nm-wavelength light.

FIGURE 3.33: Optical images of (a, b) Bi$_2$Se$_3$ exfoliated onto deposited nickel films and of (c, d) transferred onto TEM windows and patterned with nickel wires before and after annealing to 350°C.

FIGURE 3.34: TEM analysis of Bi$_2$Se$_3$ sample with 50 nm thick Ni wires annealed to 350°C. (a) Bright-field TEM image of the flake prior to annealing (colorized). (b) STEM image of the flake prior to annealing. Red circle indicates the area selected for diffraction analysis. (c) SAED pattern of the Bi$_2$Se$_3$ flake near a wire prior to annealing, with selected area inset. Wine circles indicate the ring of Bi$_2$Se$_3$ {1120} spots. (d) EDS map of the Ni L$_\alpha$ line for the Bi$_2$Se$_3$ flake prior to annealing. (e) Bright-field TEM image of the Bi$_2$Se$_3$ flake after annealing at 350°C (colorized). (f) STEM image of the Bi$_2$Se$_3$ flake after annealing. (g) SAED pattern of the Bi$_2$Se$_3$ flake near a wire after annealing. Wine circles indicate Bi$_2$Se$_3$ {1120} spots, the green circles indicate the previously invisible {1100} first-order spots, and the teal arrows indicate some very small lattice spots that surround the second-order Bi$_2$Se$_3$ {1120} spots after annealing. (h) EDS map of the Ni L$_\alpha$ line for the Bi$_2$Se$_3$ flake after annealing.
FIGURE 3.35: TEM and AFM analysis of NiBi$_2$Se$_3$ Sample S01 after annealing to 300°C. (a) Bright-field TEM images (stitched) of S01 after annealing, colorized. (b) Dark-field TEM images (stitched) of S01 after annealing, colorized. (c) STEM image of post-anneal S01, with red circle indicating area for SAED analysis. (d) EDS maps of post-anneal S01 for the Bi$_M\alpha$ peak (top left), Se$_L\alpha$ peak (bottom left), and Ni$_L\alpha$ peak (right). (e) AFM image of S01 prior to annealing. Blurry areas are loose nickel edges from liftoff. (f) AFM image of S01 after annealing. (g) SAED analysis of S01 after annealing. Wine circles indicate the ring of \{11\overline{2}0\} spots of Bi$_2$Se$_3$, and the teal circle indicates a twinned spot.

FIGURE 3.36: TEM and AFM analysis of NiBi$_2$Se$_3$ sample S01 after annealing to 300°C, then FIB thinning in nine regions. (a) Stitched bright-field TEM images of S01 after FIB thinning. (b) Stitched dark-field TEM of S01 after FIB thinning. (c) STEM image of post-FIB S01, with thinned areas boxed by dotted white lines and areas selected for diffraction analysis circled in red. (d) EDS maps of S01 after FIB thinning for the Bi$_M\alpha$ peak (top left), Se$_L\alpha$ peak (bottom left), and Ni$_L\alpha$ peak (right). (e) SAED for the upper circled area in (c), with selected area inset. Wine circles indicate the \{11\overline{2}0\} Bi$_2$Se$_3$ spots, and teal arrows indicate the new spots that appeared surrounding the primary diffraction spots after the annealing process. (f) SAED for the lower circled area in (c), with selected area inset. Wine circles indicate the Bi$_2$Se$_3$ \{11\overline{2}0\} diffraction spots, and the teal arrow indicates an auxiliary spot. (g) AFM image of S01 after annealing and FIB thinning.

FIGURE 3.37: Analysis of change in Bi$_2$Se$_3$ sample S02 with annealing temperature. (a) STEM image (upper) and Ni$_L\alpha$ EDS map of S02 after 250°C anneal. (b) STEM image (upper) and Ni$_L\alpha$ EDS map of S02 after 275°C anneal. (c) STEM image (upper) and Ni$_L\alpha$ EDS map of S02 after 300°C anneal. (d) AFM image of S02 prior to annealing.
FIGURE 3.38: TEM and AFM analysis of NiBi$_2$Se$_3$ sample S03, annealed to 325 °C. (a) STEM image of S03 post-anneal, showing asterisk-shaped (*) pattern radiating outwards from central nickel patch. (b) SAED image of lower left corner of S03, partially covered by Ni thin film post-anneal. Wine-colored circles indicate Bi$_2$Se$_3$ \{11\overline{2}0\} spots, and green circles indicate the faint \{1100\} spots that appeared after the anneal. (c) AFM of S03 before annealing was performed. Blurry areas are due to loose edges on the Ni patches due to liftoff. (d) AFM of S03 after 325 °C anneal. (e) EDS of NiL$_\alpha$ peak of S03 after anneal, showing clear disruption of the central Ni patch and areas of high concentration throughout the sample. (f) AFM detail of the central Ni patch of S03. (g) EDS detail of the central Ni patch of S03, showing that areas of higher Ni concentration follow the asterisk symbol and appear to often follow lattice vectors.

FIGURE 3.39: Diffraction, AFM, and EDS analysis of NiBi$_2$Se$_3$ sample S04, annealed to 310 °C. (a) STEM images (stitched) of S04 after annealing. (b) SAED of gold-circled area in (a). Wine-colored circles indicate the \{11\overline{2}0\} diffraction spots of Bi$_2$Se$_3$, green-circled spots are the \{1\overline{1}00\} spots that seem to only become visible after annealing, and teal arrows indicate the small spots that surround the second-order Bi$_2$Se$_3$ \{11\overline{2}0\} spots. (c) SAED of the teal-circled area in (a). In addition to the markings described in (b), the gold-circles indicate a new band of small, faint spots that appeared in this nickel-heavy region. (d) SAED of the teal-circled area in (a). Markings are as described in (b). (e) SAED of the green-circled area in (a). Markings are as described in (b). (f) SAED of the violet-circled area in (a). Markings are as described in (b), but the green spots have split considerably such that they form bands. (g) AFM topography of S04 post-anneal. (h) EDS map of the NiL$_\alpha$ line for S04. Colored circles indicate the same regions as in (a). 

FIGURE 3.40: EDS analysis of upper tip of Bi$_2$Se$_3$ sample S04 after 310 °C anneal. White arrows indicate a few features that are shared across all maps. (a) Total counts EDS image (stitched). (b) BiM$_\alpha$ EDS map (stitched). (c) SeL$_\alpha$ EDS map (stitched). (d) NiL$_\alpha$ EDS map (stitched).
FIGURE 3.41: Before and after optical images of Bi$_2$Se$_3$ flakes exfoliated onto 50 nm iron thin films and then annealed. (a) and (b) are from different samples.

FIGURE 3.42: Optical and TEM microscopy of Bi$_2$Se$_3$ annealed with niobium. (a) Low-magnification TEM image of Bi$_2$Se$_3$ flake annealed to 450°C with Nb leads. (b) Optical images (100x) of Bi$_2$Se$_3$ exfoliated onto 50 nm Nb film before annealing. (c) 100x image of same sample as (b) after 300°C anneal, showing no discoloration of the Bi$_2$Se$_3$ flakes. (d) SAED pattern of region 1 in (a), with selected area inset. The violet circle indicates the \{200\} spots, the gold circles indicate the \{121\} spots, and the dark pink circle indicates the \{042\} spot of a bcc lattice viewed down the [012] zone axis. (e) SAED pattern of region 2 in (a), with selected area inset. Green circles indicate the Bi$_2$Se$_3$ \{1\bar{1}00\} spots, wine circles indicate the Bi$_2$Se$_3$ \{1\bar{1}20\} spots, the teal arrows indicate new structure that appears around the primary spots, and the gold circles indicate additional faint lines of spots that appear between the primary second-order spots. (f) HR-TEM pattern of area that retains six-fold rotation symmetry, with FFT inset. In the FFT, the wine circles indicate the \{1\bar{1}20\} Bi$_2$Se$_3$ spots. (g) SAED of region 3 in (a), with selected area inset. The violet circles indicate the \{200\} spots, and the light blue circles indicate the \{1\bar{1}0\} spots of a cubic or tetragonal lattice viewed down the [001] zone axis. (h) HR-TEM of area that exhibits four-fold rotation symmetry, with FFT inset. The violet and light blue circles indicate the same spots as in (g).

FIGURE 3.43: EDS maps of the NbBi$_2$Se$_3$ flake annealed to 450°C, showing (a) Bi M$_\alpha$, (b) Se L$_\alpha$, and (c) Nb L$_\alpha$. 
FIGURE 4.1: Exfoliation of ultrathin VSe$_2$: (a) Exfoliation setup, including 3D-printed cuvette holder (CAD inset), glass cuvette containing propylene carbonate, tetrapropylammonium chloride, platinum electrode, and titanium hook electrode holding bulk VSe$_2$ crystal. The crystal turns black when the intercalation process begins to separate individual layers. (b) Propylene carbonate containing suspended ultrathin VSe$_2$ flakes (top left), atomic structure of single 1T–VSe$_2$ unit cell (top right), and structure of three VSe$_2$ layers (bottom). (c) Optical image of exfoliated VSe$_2$ flakes drop cast onto Si/SiO$_2$ wafer fragment.

FIGURE 4.2: 3D printed tip and sample magnetizer and transfer arm. The magnetizer is printed from blue nylon, and the transfer arm is printed from black ABS plastic. The design of the magnetizer allows for a field either coplanar with the sample or MFM cantilever (as shown) or perpendicular to the material when tipped on its side. The 3” x 1/4” N45 sintered NdFeB magnets (13500 G, 70 lbs pulling force, CMS Magnetics) are super-glued in place to prevent them from flying off the printed base and sticking to both each other and any nearby ferrous metal and are labeled for safety.

FIGURE 4.3: Image of post-anneal oxidized VSe$_2$ at 50x magnification (scalebar unavailable). The orange color indicates the presence of VO$_2$.

FIGURE 4.4: (a) Optical image of unannealed VSe$_2$ sample prepared by mechanical exfoliation. VSe$_2$ flakes can be seen primarily in the red circled region, but there is one blue-tinted silver flake in the upper right quadrant of the image, and a few thinner flakes at the bottom below the red circle. Other features are predominantly adhesive stains. Scale bar is 10 µm. (b) AFM image of the thinnest flake of mechanically-exfoliated VSe$_2$ located after many trials.

FIGURE 4.5: AFM topography of electrochemically exfoliated VSe$_2$ flakes treated with (a) pure ethanol, (b) 3 mM FDT in ethanol, (c) 5 mM FDT in ethanol, and (d) pure FDT at roughly 0 h (top) and 24 h (bottom). Note that the scale is capped at 20 nm for consistency and visibility of the thinnest VSe$_2$ flakes.
FIGURE 4.6: Topography of electrochemically exfoliated VSe$_2$ flakes dried using an Edwards nXDS 6i scroll pump, treated with 5 mM FDT, and measured the same week as preparation. (a) Flakes measured immediately after removing from vacuum. (b) Flakes measured approximately 24 hours after removing from vacuum.

FIGURE 4.7: MFM phase measurements of VSe$_2$ flakes treated with (a) pure ethanol, (b) 5 mM FDT in ethanol and (c) pure FDT at roughly 0 h (top) and 24 h (bottom). In (a), the features in the top quarter of the 24-hour image are not associated with any topography and are suspected to be spurious instrument fluctuations. In (c), note that after passing over a high feature in the approximate center of the first scan, the contrast inverted at the horizontal line. The contrast in the upper part of the image has been inverted back for easier viewing.

FIGURE 4.8: (a) Tapping mode AFM, (b) TR-MFM, and (c) MFM scans of a VSe$_2$ bare flake prepared by electrochemical exfoliation.

FIGURE 4.9: TEM and Raman analysis of bare electrochemically-exfoliated VSe$_2$ ultra-thin flakes. (a) Room-temperature HR-TEM of suspended thin VSe$_2$ showing a lattice spacing of 0.337 nm. (b) Room-temperature selected-area electron diffraction of suspended thick VSe$_2$ with simulation inset. (c) 87.8 K HR-TEM image of suspended thin VSe$_2$ with a lattice spacing of 0.332 nm. (d) EDS spectrum of bare VSe$_2$ on holey carbon grid, showing vanadium and selenium as well as a miniscule sulfur peak, but no fluorine. (e) Raman spectra of thick (red) and thin (blue) bare VSe$_2$ flakes on Si/SiO$_2$ wafer fragment.
FIGURE 4.10: Oxidation damage and both naturally-occurring and deliberately-sculpted structures appearing in bare VSe$_2$ with approximately 12 h air exposure. (a) Low-magnification image of air-exposed VSe$_2$ flake over carbon grid. Bare, unoxidized flake shown in inset for comparison. (b) HR-TEM image of oxidized region adjacent to crystalline VSe$_2$. Crystalline region has lattice spacing of 0.35 nm. (c) “Nanobridge” found in damaged region of air-exposed VSe$_2$, showing a lattice spacing of 0.45 nm. (e) Edge of a pore drilled by rapidly bringing the beam to crossover in bright-field TEM mode. There is approximately 5 nm of amorphous material between the pore itself and crystalline hexagonally-symmetric VSe$_2$ with a lattice spacing of 0.31 nm.

FIGURE 4.11: Analysis of passivated VSe$_2$. (a) Phase-contrast TEM of suspended VSe$_2$ treated with pure FDT. Extensive carbon contamination can be seen from higher-magnification imaging (dark circles), STEM spot mode (black ovals), and beam damage. (b) SAED pattern of 5 mM FDT-treated thin VSe$_2$ flake. (c) HR-TEM image of suspended VSe$_2$ flake treated with pure FDT. Amorphous regions due to carbon contamination of the surface are abundant, but it is possible to obtain a lattice spacing of 0.382 nm from non-covered areas of the sample. (d) EDS spectrum of 5 mM FDT-treated sample post RTA, showing vanadium, selenium, potentially oxygen (O K cannot be resolved from V L), as well as small fluorine and sulfur peaks. (e) comparison of bare (red) and 5 mM FDT-treated (blue) VSe$_2$ Raman spectra.

FIGURE 4.12: (a-f) EDS mapping of unannealed VSe$_2$ flake treated with 5 mM FDT in ethanol. (g) EDS spectrum of the same flake, demonstrating the extensive carbon contamination compared to the signal from the VSe$_2$ flake.

FIGURE 4.13: TEM and EDS of VSe$_2$ from 2-day-old solution. (a) Low-magnification image of VSe$_2$, showing the beginnings of a tear. (b) HR-TEM image of aged VSe$_2$, showing a lattice spacing of 0.336 nm. (c) HR-TEM image of the edge of the tear in the VSe$_2$ flake, which continued to expand quickly during imaging. (d) EDS spectrum of aged VSe$_2$ flake, showing carbon, oxygen, vanadium, and selenium.
FIGURE 4.14 : TEM analysis of nanowires and porous chunks that form in two-day-old VSe$_2$ suspension in PC. (a) Low-magnification image showing VSe$_2$ flakes, Se nanowires, and vanadium-enriched chunks. (b) HR-TEM image of Se nanowire with a lattice spacing of 0.45 nm. (c) FFT of nanowire shown in (b), demonstrating rectangular symmetry. (d) Dark-field STEM image indicating region of nanowire selected for EDS analysis (red box). (e) EDS map of nanowire vanadium signal. (f) EDS map of nanowire selenium signal. (g) Dark-field STEM image indicating region of porous chunk selected for analysis (red box). (h) EDS map of chunk vanadium signal. (i) EDS map of chunk selenium signal.

FIGURE 4.15 : Additional images of chunks that formed in 2-day-old VSe$_2$ PC suspension. (a) Bright-field STEM image of a large chunk resting atop an ultrathin VSe$_2$ flake, with dark-field STEM image inset. (b) Zoomed-in bright-field TEM image of chunk featured in (a). (c) Bright-field STEM image of a very large chunk connected to the copper grid and surrounded by several large VSe$_2$ ultrathin flakes, with dark-field STEM image inset. (d) High-resolution TEM image of part of a chunk, with FFT inset.

FIGURE A.1 : (a) Single-chip design for 20-lead wafer pattern. (b) Dose test lithography pattern with dose factors for the test listed on the sides (outer, inner).

FIGURE A.2 : (a) Wafer-scale design for the 12-lead 3 mm $\times$ 4 mm chips with SiN$_x$ windows. (b) Single-die design for 12-lead window chips.

FIGURE A.3 : (a) Wafer-scale design for the 16-lead 2.4 mm $\times$ 3.8 mm chips with SiN$_x$ windows. Note the quality of life feature on the pads mask of arrows on the edges directing the user to the location of the alignment marks. Since the pads are patterned first, these features will be visible during back-side alignment for the TEM windows. (b) Single-die design for the 16-lead window chips. (c) Central detail of the 16-lead window chips, showing additional alignment marks.

FIGURE B.1 : TEM sample stage for 2 mm $\times$ 4 mm SiN$_x$ window chips that I designed and was made in the David Rittenhouse Labs machine shop from lead-free brass.
FIGURE B.2: Sample clip for 2 mm × 4 mm TEM stage that I designed and which was made from spring bronze by the David Rittenhouse Labs machine shop. 139

FIGURE B.3: Brass holder I designed along with Jerome Mlack (who 3d printed the original part) for the micromanipulator for the transfer stage so that it could be securely mounted on a lab jack. 140

FIGURE B.4: Brass platform I designed along with Jerome Mlack (who 3d printed the original part) for the sample arm in the microscope transfer stage. Threaded 1/4" bolt holes are provided for the transfer arm itself to be mounted securely in place, but we typically used a large binder clip instead, as it allowed for more freedom to reposition the arm as necessary. 141

FIGURE B.5: Diagram of the cuvette holder for electrochemical exfoliation. Measurements are in mm. Cuvette holder was 3D printed from ABS plastic with an infill of 50%. The outer cage of the holder is 25 mm wide and has square “legs” that are 6.25 mm wide. The total width of the cage is 25 mm. In the center of this structure, there is a square cutout with side length 13.5 mm that extends from the top of the structure down into the base. This cutout securely holds the cuvette and prevents it from sliding or tipping within the cage. 142
FIGURE B.6: Design of the breakout box that I drafted, machined, and built for the probe station and other transport measurement apparatuses. The left set of connections is for triaxial TNC cables, as are installed in the probe station, and the right set of connections is for biaxial BNC cables. Inputs and outputs are connected via double-pole double-throw (DPDT) switches that are set to on (connected), float (instrument grounded, DUT floating), and ground (instrument and DUT grounded). To avoid ground loops, the ground is set up as a star ground with a common copper strip. The TNC bulkheads are connected to banana jack binding posts to interface with the Keithley 6221/2182A stack, which use alligator clips and spades to connect. The TNC bulkheads are also connected to a second set of DPDT switches so that the sheaths may also be grounded or connected to a guard voltage for shielding. Effort was made to ensure that all component terminals were made from either gold- or silver-plated copper to minimize thermoelectric EMFs and contact resistances; connecting wires were made of unplated copper; and Kester cryogenic solder (which had the smallest difference in work function compared to copper) was used to secure connections. Due to the high lead content of this solder, the breakout box is likely not ROHS-compliant.
CHAPTER 1 : Introduction

1.1. Topic and Context

Generally, human society has a voracious appetite for increasing, faster, and more energy-efficient computational power in order to meet the large-scale data acquisition, storage, and analysis requirements of modern science, industry, financial, business, and entertainment sectors with minimal energy costs to both the user and the environment. As Moore’s law begins to bump up against the physical limitations of silicon-based transistors and as long-term high-volume data storage becomes increasingly important in “big data” applications, a type of computing known as spintronics may help meet the need. In addition, quantum computing holds the promise to be able to ensure secure communications\(^1\) and solve a variety of important problems more quickly or more accurately than is possible with classical computers, such as in simulations of chemical reactions\(^1\).

Spintronics itself is already a reasonably well-developed technology with widespread integration of technologies ranging from decades-old magnetic hard drives to more recent magnetic RAM (mRAM) devices, but work in miniaturization and efficiency improvements are continuing, and there remains the possibility of incorporating 2D materials and topological insulators for improved performance or exotic effects. On the other hand, quantum computing is a rapidly-developing field with many competing implementation options with their own benefits and drawbacks. The method that caught my interest was fault-tolerant topological quantum computing, which can incorporate 3D topologically insulating materials.

I was able to combine these two subjects in my research by pursuing two main thrusts: materials analysis, alloying, and sculpting of layered Van der Waals material and topological insulator bismuth selenide (Bi\(_2\)Se\(_3\)), and preparation, passivation, and defect investigation of in-plane layered ferromagnet vanadium selenide (VSe\(_2\)) with an eye towards quantum devices and unified applications in spin-orbit based spintronic memory.

\(^1\)And also break previously secure communications, but that’s happening anyway, so why not try to be first.
1.2. Relevance and Importance

1.2.1. Introduction to Topological Insulators

Topological insulators are a novel class of materials first predicted by Kane and Mele in 2005. Topological insulators have insulating states within their physical bulk, and they have highly-conductive states on their physical surfaces that are protected against disorder by time-reversal symmetry. These surface states are spin-polarized, which means, among other things, that backscattering from these states is strongly suppressed, as an electron would need to flip its spin to travel in the other direction, and that the surface states effectively have perfect spin-orbit coupling. The surface states of these materials exist at room temperature and above, as the protection offered by time-reversal symmetry is not broken by disorder, but only by conditions such as the presence of a perpendicular magnetic field. Therefore, one of the more mundane potential applications of topological insulators is as extra-high conductivity electronic interconnects. On the other hand, the ability to generate perfectly spin-polarized currents makes topological insulators extremely attractive for spintronics. In addition, when the surface of a topological insulator is proximatized by a superconductor, it forms a state capable of hosting Majorana bound states, which are virtual anyons that can be physically manipulated relative to each other in such a way that they can perform quantum computational operations via what are known as braiding operations.

1.2.2. Introduction to Ferromagnetism in Spintronics

Spintronics are computational devices in which spin states are manipulated to perform calculations or store information (i.e., “spin electronics”). There are two primary ways that this can be approached, which are complementary and can be incorporated within a single device. The first is to control electronic transport using spins, as is the case in spin valves and devices that exploit magnetoresistive effects. The second method is to control spin transport using electric fields, which occurs in spin torque-based devices. Spintronics is a promising tool for modern computation because its features include low-power ultrafast switching, nonvolatile memory with minimal refreshing requirements, and an immunity to radiation bit flips that makes it potentially very useful in space-based applications.

One of the most basic spintronic devices is known as the spin valve, which is composed of two
ferromagnetic layers separated by a thin layer of a normal metal. Spin valves are magnetoactive devices which exhibit either a high or a low resistance state based on whether the two ferromagnetic layers are aligned or antialigned through an effect known as giant magnetoresistance, or GMR. The change in resistance is due to spin-dependent scattering in ferromagnets. When the two layers are antialigned, an electron originating from and possessing the same spin polarization as the first FM layer with the same spin polarization (or opposite magnetization) as the first layer will become a minority spin carrier in the second FM layer and encounter a higher density of available states above the Fermi level in the antialigned layer, which leads to a higher scattering probability. The primary figure of merit for spin valves and other magnetoresistive devices is the on-off ratio \( R_{on}/R_{off} \). In GMR devices, the on-off ratio is typically about 0.1. GMR spin valves are an extremely well-established technology that notably have been used for magnetic hard drive read heads.

The next step up in device complexity is the magnetic tunnel junction, or MTJ. Instead of the ferromagnetic layers surrounding a layer of normal metal, as in a GMR device, the ferromagnetic layers are separated by an ultrathin insulating barrier, which blocks the flow of classical current. The current that passes through the device is instead a quantum tunneling current. In ferromagnetic materials, the tunneling current is also spin-dependent due to the spin-based difference in the density of states. When the two ferromagnetic layers are aligned, the origin and destination of the minority spin carriers are both large, partly-filled bands, which means that many electrons at the Fermi level will have the opportunity to tunnel and that there are many available states for them to occupy on the other side of the insulating barrier. On the other hand, in the antialigned configuration, the spin minority carriers on one side are spin majority carriers on the other, so spin minority carriers “attempting” to tunnel across the barrier will “see” a much smaller number of available states, which dramatically reduces the tunneling probability. While MTJs are capable of functioning in much the same capacity as GMR spin valves and have been implemented as such, their on-off ratio is superior, beginning around 1 to 2, or at least a factor of two. In addition, MTJs have considerably higher input impedance, and both of these features make MTJs better suited for sensing applications and interfacing with electronics.

While traditionally external magnetic fields have been used to change the alignment of MTJ and GMR devices, in second-generation spintronics an effect known as spin-transfer torque (STT) is instead employed. Spin-transfer torque arises when spin-polarized electrons interact with a magnetic
material that they are not aligned with. The nonaligned magnetization acts to rotate the spins so that they come into the energetically-favored orientation, but because this realignment requires a torque be exerted upon the spins, the spins exert an opposing torque on the surrounding material itself due to Newton’s laws\(^8\). In magnetoresistive junctions that are aligned, passing electrons from a magnetically soft “free layer” to a magnetically hard “fixed layer” via an applied current causes an accumulation of spins in the free layer that are not aligned with its magnetization, as the aligned spins preferentially travel into the fixed layer\(^2\). In an appropriately-engineered system, the relaxation of these spins can exert enough torque to either generate stable precession of the free layer magnetization, which can be used as a DC-based tunable microwave oscillator, or flip the magnetization entirely, which is useful for switching devices such as MRAM. In an antialigned system, reversing the direction of the applied current will reverse the direction of the spin torque and can bring the two layers back into alignment\(^8\).

The efficiency parameter for STT-MRAM is \(I_s = \frac{\hbar}{2e} P I_c\), where \(I_s\) is the spin current in the free layer, \(I_c\) is the spin-polarized charge current, and \(P\) is the spin polarization of the fixed layer\(^12\). STT-MRAM has already reached commercial application for nonvolatile memory storage without the need for battery backup power or uninterruptable power supplies, but it faces a tricky optimization challenge: for optimal write speed and most reliable switching, \(I_c\) should be high; for optimal memory density, and ease of switching the size of the device should be small; and for optimal energy efficiency, and device endurance, the applied voltage should be low.\(^11\) It is obvious that the demands of write speed and reliability come into conflict with the demands of energy efficiency and endurance\(^3\), however the device size design factors also introduce their own complications. Reducing the device size reduces the current necessary to flip the bit, which obviously reduces the power consumption of the device and the strain on the tunneling barrier, but it also reduces the energy necessary to flip the bit. This reduced energy barrier decreases a parameter known as the thermal stability factor, which measures how difficult it is for thermal fluctuations and applied currents below the critical \(I_c\) to flip the bit\(^8,11\). As the device size decreases, it becomes increasingly vulnerable not just to thermal fluctuations, but also to read disturbance, which is the phenomenon in which applying the read current to measure the magnetoresistance actually writes the bit\(^12\).

\(^2\)Reflection from an interface can also generate spin torques, which is important for MTJs.
\(^3\)Modern STT-MRAM devices operate at about 3.3 V, which is considerably higher than SRAM, but considerably lower than the 15 V to 20 V required by NAND Flash memory.
A workaround for the dilemma presented by STT-MRAM scaling is presented by the development of spin-orbit torque MRAM, or SOT-MRAM. While STT-MRAM is a two-terminal device, SOT-MRAM has three terminals. While it may not be immediately apparent why an extra electrode circumvents the issue of read disturbance, SOT-MRAM's device geometry and principle of operation makes it clear. SOT-MRAM is based on the Spin Hall Effect, in which materials with strong spin-orbit coupling that transmit conventional currents exhibit spin accumulation on their physical surfaces transverse to the direction of current flow. Two of the terminals of SOT-MRAM are composed of a strip of strong spin-orbit coupling material, which forms the write line for the device. The third terminal connects to the fixed layer of an MTJ that is attached to the write line. When a charge current is passed through the write line, the spin accumulation due to the Spin Hall Effect applies a torque to the free layer of the MTJ, which in turn perturbs the magnetization of the free layer and can flip the bit. The read line, on the other hand, measures the resistance across the MTJ and one of the write line terminals. The spin current generation efficiency for SOT-MRAM is given by $I_s = (\frac{\Delta s}{2e}) \frac{L}{t} \theta_{SH} I_c$, where $L$ is the size of the MTJ, $t$ is the thickness of the Spin Hall layer, and $\theta_{SH}$ is the Spin Hall angle. Unlike the magnetic polarization, $\frac{L}{t} \theta_{SH}$ can be greater than 1 with proper engineering, so much smaller currents can be used to write the device. Additionally, the MTJ itself can be made so that it performs poorly as an STT device, which helps inure it somewhat against read disturbance. The increase in spin current generation efficiency and the fact that the spin torque is applied by passing current through a conductive metal rather than an insulating junction means that SOT-MRAM can operate at below 1 V. In addition, switching times can go as low as 500 ps without needing to increase the write current.

2D materials in spintronics bring much of the same promise they do to other fields of electronics: improved miniaturization, increased surface-to-volume ratio for better cooling and interactions with materials at interfaces, and the potential for novel electronic states, and in this case novel spin textures. On the other hand, as mentioned briefly in Section 1.2.1, the surface states of topological insulators effectively have perfect spin-orbit coupling, which makes them highly attractive candidates as spin generators and as the write line for SOT-MRAM, especially those topological insulators that also have high conductivity in the bulk states.
1.3. Objectives

Objectives for the Bi$_2$Se$_3$ project centered around advancing knowledge of both the effects of alloying with Group 10 metals and on the feasibility of particle beam dry-milling techniques for nanosculpting complex device geometries. It was shown in Mlack et al.\textsuperscript{15} that Pd contacts react extensively with Bi$_2$Se$_3$ upon annealing to form a superconducting compound. For my part in it, I sought to determine the identity and structure of the superconducting compound, elucidate the extent of the reaction, and determine if there was any way to make the reaction more controllable. A secondary objective of my work was to determine if related metals, such as Ni may also react with Bi$_2$Se$_3$, as well as certain desirable metals such as the superconductor Nb, the ferromagnetic metal Fe, and W, out of ready availability.

My research goals for VSe$_2$ primarily focused on the development of the Drndić lab’s capabilities for producing and handling the material, as well as developing my newly-conceptualized technique for direct imaging of lateral magnetic fields: torsional resonance magnetic force microscopy (TR-MFM). Thus, I first explored the limits of mechanical exfoliation using a variety of adhesive tapes, then sought to flesh out the parameters and capabilities of a recently-reported electrochemical exfoliation technique. From there, I investigated the air-stability of my prepared VSe$_2$ under various passivation treatments, provided material characterization, and worked out our lab’s procedure for studying ferromagnetic nanomaterials via cryogenic Lorentz TEM.\textsuperscript{4}

1.4. Overview

In Chapter 2, I outline the methodology and equipment I used to pursue my research. Section 2.1 first covers the basic optical and electron beam (e-beam) lithographic techniques I used for producing wafers and devices for transport measurement, materials analysis, and and \textit{in situ} TEM experiments. Next, the apparatus and procedures for 2D material stamping transfers using poly(methyl methacrylate) (PMMA), poly(dimethylsiloxane) (PDMS), and poly(propylene carbonate) (PPC) are described. Section 2.1 also details equipment and procedures for handling air-sensitive materials such as VSe$_2$. Next, Section 2.2 is dedicated to equipment and techniques for materials analysis, including transmission electron microscopes (TEMs), their operational modes, cryogenic, magnetic,\textsuperscript{4}Transport measurements were also planned, but never accomplished due to the ARS probe station’s stubborn refusal to function consistently, but that’s a separate tragedy. Useful lessons from the baleful tale of the probe station, as well as an SOP and troubleshooting steps, may be found in Chapter 2.
and and in situ transport techniques; Raman spectroscopy and mapping; and atomic, magnetic, and torsional resonance magnetic force microscopy (AFM, MFM, and TR-MFM, respectively). Finally, Section 2.3 provides the operational procedure and troubleshooting steps for the Drndić lab’s cryogenic probe station, and briefly describes the software I wrote for controlling instrumentation for the probe station and other transport setups in the lab.

In Chapter 3 I report the results of my investigations into topological insulator Bi$_2$Se$_3$. A more detailed introduction to topological insulators, their properties, applications, and challenges is presented in Section 3.1. The material effects of focused ion beam (FIB) and TEM nanosculpting on Bi$_2$Se$_3$ as well as the feasibility of these methods for continued research and advanced device production are summarized in Section 3.4. Finally, Section 3.5 focuses on the results of my experiments regarding the formation, extent, and structure of alloys between Bi$_2$Se$_3$ and various metal contacts.

Chapter 4 centers around my efforts into initiating a new research project concerning in-plane two-dimensional ferromagnetic materials (2DFMs) within the Drndić lab. Section 4.1 contextualizes the project by discussing the discovery and recent history of 2DFMs, particularly vanadium dichalcogenides VS$_2$ and VSe$_2$ (my research focus) as well as an overview of proposed applications for VX$_2$ nanomaterials. Details of my work into production, properties, and stability of VSe$_2$ are provided in Section 4.2. Results appear in Section 4.3 and are analyzed in Section 4.4.

Finally, Chapter 5 discusses the main conclusions of my work, my contributions to the scientific capabilities of the University of Pennsylvania, and proposes avenues for future study.
2.1. Basic Fabrication

2.1.1. Optical Lithography

Because the chips for both the 8-lead Hummingbird TEM transport holder and the old He-3 fridge needed to be smaller than the Drndić lab’s previous 6-lead transport chips, and have more electrodes, one of my tasks was to create new optical lithography masks for both patterning the electrodes and making TEM windows and score lines. After consultation with the staff at the Singh Center’s Quattrone Nanofabrication Facility and Jacob Swett of Oxford University, I also decided to modify the lithography process to take advantage of the fabrication bay’s capability for back-side alignment. CAD of the masks I designed can be found in Appendix A. Because the process I developed differs from the Drndić lab’s, I report it in full here. The process for patterning electrodes works on silicon wafers coated in either low-stress SiN$_x$ or SiO$_2$, but the masks and process for score lines and TEM windows should only be used on double-side polished (100) silicon wafers with a coating of low-stress SiN$_x$. If there is an oxide layer between the silicon and the silicon nitride, a buffered oxide etchant (BOE) step should be added before the K$_0$H etch.$^5$

The first step in the lithography process is, cleaning and degreasing. This is a very important step and should not be skipped, even with completely fresh and new wafers.

To clean and degrease the wafers, first fill a dish that can hold the entire wafer with acetone and a second dish that can hold the entire wafer with either methanol or isopropanol.$^6$ The wafer should then be immersed in the acetone and agitated lightly for 5 min. If delicate structures such as SiN$_x$ windows are not present, it can be sonicated for extra effect during this time. Then, remove the wafer from the acetone, and rinse both surfaces with an acetone wash bottle into either a solvent cup sink or into the acetone dish.

While the wafer is still wet, quickly transfer it to the methanol (or isopropanol) dish and immerse it for 5 min. If the wafer is safe to sonicate, you may do so. While this soaking is occurring, use a cleanroom wipe to clean the interior surfaces of the wafer holder (tray, spring, lid) so that

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$^5$I cannot report on this process, as I have specifically avoided working with HF.

$^6$Isopropanol is less toxic, but methanol has slightly superior performance and dries slightly cleaner.
transporting the wafer does not re-contaminate it. Additionally, empty and thoroughly rinse the acetone dish and then fill it with deionized (DI) water. When the timer is finished, remove the wafer from the alcohol of choice and rinse both sides of the wafer with the alcohol.

While the wafer is still wet with the alcohol, quickly transfer it to the dish of DI water and and allow it to soak or sonicate for another 5 min. Then, remove the wafer from the water dish and rinse both sides thoroughly with more DI water. Finally, use a N$_2$ gun to dry the wafer from top to bottom, first the front side and then the back, and doing your best to propagate a uniform front of water. During this time, it may also be necessary to dry the wafer tweezers, as they can hold beads of water that are otherwise difficult to remove from the wafer.

The optical lithography masks should be cleaned by repeating the acetone and methanol/isopropanol steps from the wafer, but reducing the time to 2 min, and then using the N$_2$ gun to dry. If the mask is not clean after this process, a strip in N-methyl-2-pyrrolidone (NMP) should be used, followed by a rinse in acetone and then methanol.

In order to fully dry the wafer and improve its adhesion with the Shipley positive-tone resists (S18 series), the wafer should next be placed in the YES Vapor Deposition System and the recipe for hexamethyldisilazane (HMDS) priming run. This step takes 20 min to 30 min. Make sure to use the provided potholders/oven mitts to remove the wafer tray from the YES oven, as it will be hot. Finally, use an N$_2$ gun to remove any bits of dust that may have landed on the wafer before proceeding to the rest of the lithography process.

Because the electrodes patterned on the front side of the wafer are fairly dense and small, using lift-off resist (LOR) will improve the results. LOR is a base layer of resist that has a faster dissolution rate in developer solution, so when paired with a standard positive-tone resist, it is able to create an undercut much like those produced by negative-tone resists. An undercut in the resist means that during metal deposition, the electrodes are disconnected from the rest of the metal film, which means a cleaner liftoff with no jagged edges or parts of the pattern being pulled off the wafer. For my process, I use LOR 3A, and my recipe yields a film of approximately 0.31 µm. This layer should be 1.2 $\times$ to 1.3 $\times$ the thickness of the metal layer to be deposited for optimal results. Additionally, before use the LOR 3A bottle should be left to sit loosely covered for 15 min before use to allow for
In order to spin the layer, program the spinner to rotate at 500 RPM for 5 s and then at 3500 RPM for 45 s. Then, center the wafer on the spinner and evenly coat it with LOR 3A using a pipette, working from the center outwards. Use the pipette to remove any visible bubbles in the resist, and then run the spin program. Then, bake the wafer at 180 °C for 5 minutes on a hotplate and inspect the film for any defects that may look like comets, dots, or streaks. If there are a large number of film defects, or any that are particularly large, strip the resist and try again. Otherwise, use the N2 gun to blow off any new dust that may have settled and proceed to applying the positive resist layer.

For the positive resist, I used Shipley S1813, which is able to provide appropriate resolution and film thickness for the pattern. The positive resist layer should be at least 3 × the thickness of the deposited metal film, and this recipe yields a film of approximately 1.3 µm.

First, allow the S1813 bottle to rest loosely covered for 15 min to allow for outgassing and for particles to settle and program the spinner for 500 RPM for 5 s and then 3500 RPM for 45 s. Then, load the wafer on the spinner and use a pipette to evenly dispense the resist on the surface of the LOR film, working outwards from the center and ensuring there are no gaps. Again, use the pipette to remove any visible bubbles. Run the spinner, and then bake the wafer on a hotplate at 115 °C for 1 min. Once again, spray down the wafer with the N2 gun and inspect the film for defects. If there are a large number of defects or any particularly large ones, strip the resist and try again.

The next step is mask alignment and UV exposure, which I performed in the SUSS MicroTec MA6 Mask Aligner. Because this is the first layer of optical lithography, the “non-alignment” procedure for operating the MA6 should be used9. For this process, the recipe “Drndic S1818” should be loaded, and the following settings should be verified:

Because this is a two-step lithography process, it is very important to ensure that the wafer flat is flush against the pins in the mask aligner so that both the leads and the score lines align with the cleaving planes of the wafer. Additionally, ensure that the lithography mask itself is inserted such

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7 You could also skip this step if you have a filter pipette to use.
8 To be clear, this strips all of the resist, not just the S1813 layer.
9 The SOP for the MA6 Mask Aligner in the Singh Center may be found at https://www.seas.upenn.edu/~nanosop/MA6_SOP.htm
WEC Mode: Contact
WEC Offset: 0 \mu m
Exposure Mode: Constant Dose
Exposure Time: 5 s
Dose: 70 mJ/cm^2
CD Channel: 1 (i-line)
Contact Mode: Vacuum Contact

Table 2.1: MA6 exposure parameters for LOR 3A/S1813 recipe

that the alignment marks will be on the left and right of the wafer relative to the user as this is where the back-side alignment cameras are located.

After the exposure, the wafer should be developed. For this, first prepare a dish of DI water that can immerse the wafer entirely, and place it in the water sink so that when the sink is turned on, water will fill the dish. Also be sure to leave at least one sink drainage hole unblocked. Then, fill a 6" dish with just enough AZ 300 MIF developer to completely immerse the wafer. Place the wafer in the developer and gently agitate for 40 s using tweezers or a pipette or by gently swirling the dish in a circular motion. Because resist development is a very time-sensitive process, about 15 s before the timer completes, be sure to grab the wafer with wafer tweezers so that it is ready to be removed. Once the timer completes, quickly move the wafer to the DI water dish and start the sink. Allow water to flow into and out of the dish for 3 min to 5 min before turning off the sink and removing the wafer. It should one again be dried with the N\textsubscript{2} gun. At this point, the wafer is no longer critically photosensitive and can be taken to normally-lit areas. The Oxford RIE should now be used to perform a descum at the following settings:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Oxygen, 20 sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power</td>
<td>100 W</td>
</tr>
<tr>
<td>Pressure</td>
<td>60 mTorr</td>
</tr>
<tr>
<td>Time</td>
<td>30 s</td>
</tr>
</tbody>
</table>

Table 2.2: RIE descum parameters for LOR/S1813 resist.

After the descum, inspect the wafer a final time, and strip the resist and redo if the quality is poor, as after metal deposition, the wafer cannot be fixed.

For metal deposition, I use the Lesker PVD75 E-beam Evaporator (PVD-04) and run the standard recipes to deposit first 20 nm chromium and then 100 nm gold. Do not use double-sided Kapton\textsuperscript{®} tape to secure the wafer in place on the chuck, as removing the wafer from this tape is liable to
break the wafer. Instead, use the single-sided tape that is also available. When the deposition is complete, gently remove the tape using tweezers—my preferred tweezers for this have a T-shape at the end, which allows me to push the tape so it bunches up and has a more grabbable edge.

The front side of the wafer is now ready for liftoff, which is fairly straightforward. Prepare a 6” dish with either Remover PG or Microposit 1165 resist stripper in a water bath heated to 60 ºC and get a pipette\(^{10}\). Give the stripper and the water bath a few minutes to come to temperature. Place the wafer in the resist stripper and gently agitate the remover near the surface of the wafer using the pipette for 10 min, ensuring that the wafer is submerged the entire time. Do not use sonication unless absolutely necessary, as this may damage the leads. Prepare a second 6” dish of the same resist stripper. Pipette any large flakes of metal into the cup sink and then quickly transfer the wafer to the second dish. It is imperative that the wafer not be allowed to dry at all during this step, as any metal particles that are dried onto the surface will strongly adhere and be nearly impossible to remove. Place the second dish in the water bath and gently agitate the stripper near the surface of the wafer with the pipette for another 10 min. Optionally, the wafer may now be sprayed down with methanol or isopropanol and then soaked in methanol/isopropanol for 5 min which may help remove any scum that remains on the wafer as the result of incomplete photoresist removal. Next, without allowing it to dry, place the wafer in a 6” dish of DI water under the DI faucet and allow water to flow over it for 6 min to 10 min. Finally, dry the wafer using an N\(_2\) gun and inspect the wafer using a microscope in the cleanroom. If liftoff for the pattern is not complete, submerge the wafer in a dish of clean, 60 ºC Remover PG or Microposit 1165 for half an hour, rinse and clean as before, and inspect again. If the pattern is still not complete, leave the wafer in hot stripper overnight.

For the back-side process, one of the consistent issues that has needed to be addressed has been the protection of the front side of the wafer during spinning and mask alignment. The first method I tried was using Brewer Science® ProTEK® PSB coating, which effectively protected the front side from scratches but introduced an issue of its own: ProTEK® is extremely difficult to remove entirely but did peel during the KOH wet etch, and it sometimes takes the electrodes with it when it peels off. In addition, the ProTEK® consistently caused problems with establishing vacuum on the MA6, which negatively affected the alignment and exposure process. The next method I tried, which was recommended by Jacob Swett at Oxford University, was to instead use a layer of A4–450 spun on

\(^{10}\)Both PG Remover and Microposit 1165 are compatible with polyethylene materials, so the plastic pipettes in the Singh center are safe to use.
at 4000 RPM for 60 s and then hard-baked at 180 °C on a hotplate for 10 min. This layer allowed for establishing good vacuum with the MA6, but it did not protect the electrodes from scratching on the spin chuck. Therefore, my final recommendation for preparing the back side photoresist is to first clean and degrease the wafer using the steps outlined above, but do not sonicate. Then prime the wafer with HMDS in the YES oven, and then spin coat A4-450 or A4-495 polymethyl methacrylate (PMMA) on the front side using the parameters listed above. Then, using the SUSS MicroTec AS8 AltaSpray Coater (RC-01), apply a 1.3 µm-thick coating of S1813 to the back-side of the wafer. The wafer should then be baked for 60 s on a 115 °C hotplate. As usual, the resist film should be inspected for defects and should be stripped if the film is poor-quality. After the strip, PMMA should again be spun onto the front side and baked before redoing the spray coat.

For mask alignment, the back-side alignment process should be used, and the exposure parameters should be as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEC Mode:</td>
<td>Contact</td>
</tr>
<tr>
<td>WEC Offset:</td>
<td>0 µm</td>
</tr>
<tr>
<td>Exposure Mode:</td>
<td>Constant Dose</td>
</tr>
<tr>
<td>Exposure Time:</td>
<td>5 s</td>
</tr>
<tr>
<td>Exposure Dose:</td>
<td>85 mJ/cm²</td>
</tr>
<tr>
<td>CD Channel:</td>
<td>1 (i-line)</td>
</tr>
<tr>
<td>Contact Mode:</td>
<td>Vacuum Contact</td>
</tr>
</tbody>
</table>

Table 2.3: MA6 exposure parameters for back-side alignment using S1813.

Before exposure, ensure that the mask is inserted in the same orientation as the frontside mask. Also ensure that the backside pattern is less than 3 µm off in x, y, and θ from the frontside alignment marks. The entire wafer will be ruined if the score lines and windows are not aligned well with the optical leads.

The same process as above may be used to develop the back side of the wafer, or, alternatively, Microposit™ MF™-319 developer may be used for 60 s followed by wafer immersion in flowing water for 3 min.

The SiNx now needs to be stripped from the exposed regions of the back side of the wafer. The dried wafer should be carefully placed in the Oxford 80 Plus RIE with the back side facing up. The recipe “SiN etch Chen” should then be loaded. The etch rate for this recipe is about 50 nm/min + 1 min, and 100 nm of SiNx will be etched in 2 min and 30 s. After the etching program is run, the
back side of the wafer may be inspected in the ellipsometer to determine if additional dry etching needs to take place.

After the dry etch is complete, the resist should be stripped in a 6" dish of Microposit™ 1165 Remover heated to 60 °C in a water bath for 30 min. At the end of the 30 min, sonicate the wafer for 10 s, and then clean and degrease the wafer again, but do not sonicate. After drying the wafer, use an ozone plasma cleaner to give it a final clean before the KOH wet-etch.

Before proceeding with the KOH etch, realize that using the protective holder requires a 5 L beaker, and this is an enormous quantity of highly-alkaline solution. Ensure that there is enough anhydrous KOH available to make 3.5 L of 60% solution, that there is sufficient space in the alkaline waste carboy, and that you have a plan for transferring the used KOH to the waste container safely. I suggest a siphon that is started by filling it the hose with water\textsuperscript{11}. The plastic bolts holding the wafer holder together should be removed using the small plastic tool, and the wafer should be positioned inside the two o-rings with the metal facing the glass side. The wafer holder should then be put back together and sealed with the plastic bolts. You may wish to test the seal in gently flowing DI water to ensure that no liquid makes it to the front side of the wafer.

Next, place the beaker on a hotplate with a temperature gauge and fill it with 3.5 L of DI water. Clip the thermometer to the stand so that it rests in the upper-middle of the beaker and add a large stir bar. Set the speed to 100 RPM. While wearing a lab coat, nitrile gloves, and safety goggles, begin to measure out enough anhydrous KOH to make a 60% solution using the analytical balance. I found it best to weigh out \( \frac{1}{10} \) or \( \frac{1}{20} \) the amount at a time and keep track on a paper note. Before dissolving the KOH, ensure that the fume hood sash is at the minimum height possible for you to work at and that you are wearing a lab coat, base gloves, safety goggles, and a face shield. Very gradually, and while monitoring the temperature to ensure it stays below 80 °C, begin to dissolve the KOH chips in the beaker. Wait for all of the chips to dissolve completely and the temperature to stabilize below 80 °C before adding more. KOH dissolves exothermically, and if too much is dissolved at once, it can cause the solution to boil over and spill onto the fume hood and the hotplate power cables. Even worse, if the KOH cannot mix well while dissolving and the bottom of the beaker gets significantly hotter than the top, the glass can break due to thermal shock and spill 3.5 L of boiling-hot highly-corrosive solution all over the fume hood, the floor, and potentially any lab members who happen

\textsuperscript{11}It is absolutely imperative for your safety that you do not mouth-start this siphon.
to be standing nearby. A catastrophic beaker failure has happened in the Drndić lab before with a 1.5 L beaker of hot KOH, and while nobody was injured, it was a bad day. If there is a spill of any significance, contact Health and Safety for cleanup.

Once all the KOH is dissolved, set the hotplate temperature to 80°C and wait for it to stabilize. Calculate the etch rate of (100) silicon at the temperature the beaker reaches, place the back-side etching holder into the beaker and add the lid, and allow the wafer to etch for that amount of time before checking on progress. The holder will initially attempt to float until the air caught inside it can vent through the small hose. Gently agitate the holder until it will remain steady inside the solution without assistance. After the expected amount of time has passed, while wearing a lab coat and base gloves, remove the etching holder from the beaker and hold it up to the light within the fume hood while keeping your head at a safe distance. If the etch is complete, the windows should look a clear yellow or orange in the light. If the windows appear red, the etch is nearly complete. If the etch is complete, gently immerse the holder and wafer with DI water to remove residual KOH and make them safe to handle. Then, remove the wafer from the holder and use a wash bottle to rinse it with DI water. Then soak the wafer overnight in acetone or in PG Remover in a 70°C water bath for 30 min. Once again clean and degrease the wafer, but do not sonicate for any reason because it will break the TEM windows, and then use the plasma cleaner or Oxford 80 Plus RIE to remove any remaining resist residue.

2.1.2. Electron-Beam Lithography

For electron-beam lithography at chip-scale on a sample atop a TEM window, the chip should first be taped to the center of a glass coverslip using Kapton® tape on its corners. Use tweezers and great care to ensure that the tape does not cover any of the optical leads. This coverslip should then be mounted on a spin coater and the vacuum engaged. Using a pipette, a single drop of C4-495 PMMA is then dispensed on top of the chip, and the end of the pipette should be used to break surface tension. The sample should be spun at 4000 RPM for 35 s and then baked on a 180°C hot plate for 2 min. At this point a calibrated optical microscope image should be taken and then used in a program such as Layout Editor to prepare an electrode pattern. The parts of the pattern that are not on the TEM window should be separate shapes from the parts that are on the TEM window.

Potentially as high as 90°C, as the very large beaker will not maintain the setpoint temperature at all, and the thermometer cannot be used with the wafer holder.
with slight overlap, because the dose factor for the parts of the pattern that are off-window is 0.5 due to the presence of significant electron backscattering. When leads are patterned in the Johnson Lab SEM, the dose should be set to $410 \mu A \text{s/cm}^2$, the step size to 2 nm, and the probe current to slightly less than was measured at the Faraday cup per the standard operating procedure. The dose, however, is an estimate, and if the best resolution is desired, I recommend calibrating to your chips every so often with a dose test like the one shown in Appendix A.

2.1.3. Stamping Transfer

In order to use the silicon nitride TEM windows with 2D materials, it is of course vital to ensure that the 2D materials can be reliably placed onto the TEM windows. To that end, two separate methods were developed for transferring $\text{Bi}_2\text{Se}_3$, and one method was adapted with the help of Boyan Penkov of Columbia University for the accurate transfer of $\text{VSe}_2$. Designs for pieces of the transfer stage that were necessary to machine can be found in Appendix B.

2.1.4. PMMA Transfer of Bismuth Selenide

The first method for transferring $\text{Bi}_2\text{Se}_3$ relies on first exfoliating $\text{Bi}_2\text{Se}_3$ onto PMMA and then using the PMMA to transfer a selected flake to the TEM chip. A schematic of the setup for this process is shown in Fig. 2.1.

![Figure 2.1: Schematic of the stack used for PMMA transfers of Bi$_2$Se$_3$ to a 290µm chip. For clarity, the “pillars” on either side of the bottom slide are composed first one layer of double-sided Kapton® tape with the plastic covering still on, then a layer of double-sided Kapton® tape with the plastic removed, and then one-half of a glass microscope coverslip that has been broken in two. The larger glass pieces are unbroken microscope slides.]

To create Stack 1, two glass microscope slides are first adhered to each other using double-sided...
Kapton® tape. This is for structural stability. Then, towards one of the short edges, a small “pillar” is built by first placing a piece of double-sided Kapton® 1-inch wide tape that is cut to be approximately as long as half the length of a glass microscope coverslip so that the width of the tape is parallel to the short edge of the glass slide. A second layer of double-sided Kapton® is then placed atop it. Half of a glass microscope coverslip is attached. This process is repeated about 3 cm farther along the slide to create a second pillar. In between these two, another piece of double-sided Kapton® tape should be placed so that it is roughly centered in the area surrounded by the pillars and the protective plastic left on.

Stack 2: An unbroken glass coverslip should then be covered in a piece of double-sided Kapton® tape with the protective plastic left on. A square of single-sided Kapton® tape should then be placed atop the plastic square. The taped coverslip should now be placed on a spin coater, and the single-sided tape should be covered in C4-495 PMMA as if e-beam lithography were to be performed with it. The PMMA should be spun at 2000 rpm for 45 s and not baked. The single-sided tape should then be removed from the plastic and then gently pressed down on a second microscope slide so that it is roughly centered on the relative position where the central pillar is located on Stack 1. The tape should be gently stretched as it is pressed down to minimize bubbles. A gloved finger may also tap lightly, but uncareful tapping can damage the PMMA layer.

Bi$_2$Se$_3$ flakes should now be exfoliated using the blue polyamide tape until the tape is no longer tacky. It is important for the tape to not be tacky so that it does not tear the PMMA layer. Press the tape down onto the PMMA layer to transfer some of the flakes. It is safe to press a little harder to remove bubbles at this step. Gently and slowly peel back the blue tape, then check the PMMA under the microscope to ensure that it is intact and has picked up Bi$_2$Se$_3$ flakes.

Use a razor blade to remove the parts of the PMMA tape that are nonuniform—this will be apparent by bands of colors from thin-film interference. Next, place two total pieces of double-sided Kapton® tape of approximately the same size as those that formed the pillars on the first stack around the PMMA tape at the same relative positions on the slide as the pillars are on Stack 1.

Remove the plastic covering from the tape on the central pillar of Stack 1 and attach a TEM window chip (or other chip you wish to transfer Bi$_2$Se$_3$ to in a precise location) to the center of this tape.

\footnote{Be careful while breaking glass. These are easy to break, but I suggest scoring with a diamond scribe and performing the cleave on a paper towel using a stylus so that your hands are not cut if it fragments.}
Place Stack 1 on the stage of the transfer microscope. Focus on the chip, bring it into focus, center the window, and then lower the stage by several inches.

Tape the far end of Stack 2 to the end of the transfer arm and ensure that it rests securely and horizontally, then remove the plastic coverings from its double-sided tape. Use a binder clip to attach the transfer arm to the transfer arm stage (see Fig. B.4). Using the micromanipulator and the lab jack (if necessary), bring the PMMA tape into focus in the transfer microscope and find a flake that you’d like to transfer. Slowly bring the chip up to meet the PMMA, making sure to readjust the stage or the micromanipulator so that the flake is centered on the chip.

The two stacks will adhere to each other when the side pillars come into contact. Note whether or not the PMMA is in contact with the TEM window, and how tightly (the window will visibly flex if it is in tight contact), and then either lower the stage or raise the transfer arm so that the combined stack, which should be stuck to the transfer arm, can be removed. Use a razor to cut the combined stack free from the transfer arm, then inspect it in the microscope. If the flake is not in the correct spot, it is possible to attempt to remedy the situation by pushing on either Stack 1 or Stack 2 so that they slide into the correct position, but this is not always effective.

If the connection between the PMMA and the TEM window was loose, place the stack in a covered Petri dish and then move to a vacuum desiccator overnight. Allow the combined stack to relax outside the vacuum desiccator for 1 h to 1.5 h before proceeding. Next, don an additional pair of gloves or some other means of lint-free thermal protection. Bake the combined stack on a hotplate at 180 °C for 3 minutes and then remove to a paper towel. Use another glass microscope slide to press evenly down on the stack while it is still hot. Pressing unevenly may cause the flake to shift. Once the stack cools, place in an acetone bath overnight to dissolve the PMMA and adhesive and release the chip.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiN$_x$ chip</td>
<td>290</td>
</tr>
<tr>
<td>2-sided Kapton® Tape w/ Plastic</td>
<td>175.5</td>
</tr>
<tr>
<td>2-sided Kapton® Tape w/o Plastic</td>
<td>102</td>
</tr>
<tr>
<td>1-sided Kapton® Tape</td>
<td>51</td>
</tr>
<tr>
<td>Glass Coverslip</td>
<td>152</td>
</tr>
</tbody>
</table>

Table 2.4: Measured thicknesses of components used in PMMA transfer process
The success of this technique relies on closely-matched thicknesses of the three pillars, and therefore it is optimized for chips that are 290 µm thick. Table 2.4 presents the thicknesses of the different materials used in the stack, and a different stack should be calculated for a different thickness of chip. The height of the side pillars in this configuration is 458 µm, and the height of the central pillar is 443.3 µm.

2.1.5. PDMS Stamping

The second technique for 2D material transfer and positioning involves using polydimethylsiloxane (PDMS) gel. This method is considerably simpler to implement and allows for multiple attempts to be made without “committing” like with the tape stack. A schematic of the two stacks for the transfer is shown in Fig. 2.2.

For Stack 1, a square of lab-made hard-cured PDMS is first stuck to a glass microscope slide in the approximate center and then baked on a hotplate at 90°C for 5 min to encourage adhesion. This square need only be slightly larger than the chip that will then be placed atop it. Do not press the chip into the PDMS—it is sufficient for it to lightly rest atop it so that it is unlikely to slide around.

For Stack 2, cut out a square of PDMS from the center (flat) region of a #4 Gel-Pak and attach it to one end of a second microscope slide, about where the PMMA tape was placed on Stack 2 in the PMMA transfer procedure. Also bake this slide at 90°C for 5 min to help with adhesion.

Again use blue tape to exfoliate Bi₂Se₃ until the tape is no longer tacky, then press the tape into the Gel-Pak PDMS. Anneal the slide/PDMS/blue tape stack for another 5 min on a hotplate to help the Bi₂Se₃ flakes stick to the PDMS. Remove the tape and check the Gel-Pak PDMS under a microscope to ensure that flakes have adhered, and then use a square of 2-sided Kapton® tape to attach the free end of Stack 2 to the end of the transfer arm.

Align a flake to the TEM window of the chip as in the PMMA procedure in Section 2.1.4 and then bring the Gel-Pak PDMS down to meet the TEM window. It will be very obvious when the Gel-Pak PDMS makes contact, and if it does not make contact with the window itself, continue to raise the microscope stage until it does. Slowly lower the stage. If the chip sticks to the Gel-Pack PDMS, remove Stack 2 with the chip from the transfer arm and bake at 90°C for 5 min on a hotplate. If the chip does not stick, inspect the chip in the microscope because sometimes you get lucky and the
flake transfers anyway. If this is not the case, continue to try to pick the chip up with the Gel-Pack PDMS and bake on the hotplate when you succeed.

After baking, use a pair of tweezers to remove the chip from the PDMS and inspect under a microscope. If the transfer was not successful, the procedure should be tried again with the same chip and the same PDMS, although after many transfer attempts the chip will need to be cleaned.

Stack 1 may be reused indefinitely so long as it does not get dirty, and Stack 2 may be reused for about the span of a day before the PDMS should be replaced.

![Figure 2.2: Schematic of the setup used for PDMS transfers of Bi$_2$Se$_3$ to SiN$_x$ TEM windows.](image)

### 2.1.6. PPC Stamping of Vanadium Selenide

After it was determined that mechanical exfoliation was not a viable procedure for producing large quantities of ultrathin VSe$_2$ flakes, the procedure described in Section 4.2.2 was adopted. It was found that neither PMMA nor PDMS was particularly effective at picking up dropcast VSe$_2$, so a third transfer procedure based on polypropylene carbonate (PPC) stamping. This technique was taught to us by Boyan Penkov of Columbia University.

A glass microscope slide with a piece of 10:1 Sylgard™ PDMS placed in the approximate position of the PMMA tape in the PMMA transfer method in Section 2.1.4 and then annealed at 90°C for 5 min on a hotplate. A piece of Scotch® Magic™ tape (“clear tape”) should be placed over the PDMS...
so that it adheres to the glass on either side.

A wafer fragment or spare large chip should then be spun with a 1:10 PPC:Anisole ratio at 3450 rpm for 60 s to yield a film of approximately 1 µm. It should then be annealed on a 90 °C hotplate for 2 min to remove bubbles. Use a razor to nick off one corner of the film.

Next, prepare a strip of tape at least 2.5 cm long and use a hole punch to remove a circle in the approximate center. Discard the punched circle, but keep the larger tape. Apply the piece of tape to the PPC film so that the film is centered on the hole punch. Use tweezers to lift the tape and the adhered PPC film. Now, adhere the tape with the PPC to the tape covering the piece of PDMS so that the PPC film is centered over the piece of PDMS. The PPC should now be suspended and hang down when this microscope slide is turned over.

The substrate with the dropcast VSe$_2$ should now be placed on the stage of the transfer microscope, the stage temperature set to 50 °C, and a flake of interest located. Once it is centered, lower the stage. Attach the microscope slide holding the PPC to the transfer arm of the microscope, and then center the PPC. Bring the substrate back into focus and lower the transfer arm until the PPC just kisses the surface of the substrate. Raise the temperature of the stage from 50 °C to 52 °C in 0.5 °C steps. This should melt the PPC slightly so that it flows over the target flake. Slowly lift the PPC film away from the substrate, and then inspect the film to determine that it has picked up the target flake.

Change out the initial substrate for the chip the flake will be transferred to. Align the flake to the destination chip and then bring the PPC film into contact with the chip. Raise the stage temperature to 120 °C to melt the PPC film onto the chip. To remove the PPC and complete the transfer, anneal in a 1 × 10$^{-6}$ Torr vacuum oven to 350 °C$^{14}$

2.2. Material Analysis

2.2.1. TEM

A transmission electron microscope, or TEM, is a microscope that uses a beam of high-energy electrons, in my case 200 keV, to image a sample. Unlike scanning electron microscopes, which use

$^{14}$I sealed the chips with PPC transfers in Gel-Paks in vacuum bags and mailed them to Boyan at Columbia University for this step.
backscattered electrons to image samples and/or perform lithography. TEMs image using the electrons that pass entirely through the sample and substrate. The difference between scanning and transmission electron microscopes is similar to the difference between metallurgical and biological light microscopes. And, like a basic biological microscope, both samples and substrates for the samples in the TEM must be thin enough to be at least partially transparent to the incident electrons. Thankfully, many materials that are not transparent to visible light do transmit $200\text{ keV}$ electrons, including metal thin films and rocks and minerals of up to half a micron in thickness, so transmission electron microscopy is a very useful tool in mesoscopics and materials research.\textsuperscript{15} The de Broglie wavelength of $200\text{ keV}$ electrons is $2.51\text{ pm}$, so TEMs are able to image at much, much higher magnification than visible light (minimum $250\text{ nm}$) without encountering diffraction-limited resolution. In fact, top of the line TEMs are able to image individual atoms and chemical bonds with relative ease. Instrumentation can also be added to TEMs beyond the simple\textsuperscript{16} column with a field emission gun (FEG) at the top, some lenses, and an electron detector at the bottom. These instruments can aid in material characterization or introduce different factors that can affect the sample being imaged in the TEM, allowing it to be manipulated in more complicated ways or changing the local conditions for the sample, allowing direct imaging while it is in a state of flux.

Operation of the TEM is conceptually similar to optical microscopy: there is an objective lens, a focus height, different magnification settings, and bright-field, dark-field, phase-contrast, and scanning probe imaging modes. TEM microscopy is also more complicated, however, as unlike light, electrons cannot be adequately focused with physical lenses and mirrors. Instead, the electron beam is shaped using a combination of solenoid electromagnetic lenses and physical apertures, which respectively focus the beam and allow for selection of specific electrons\textsuperscript{16}. After leaving the electron source, which is a field emission gun (FEG) for both the 2010F and the F200, the beam is first collimated by the condenser lens, and the fraction of the beam to use is selected by the variable condenser aperture. The condenser aperture can select a smaller fraction of the beam either to protect a sensitive sample or to improve beam purity by omitting outer electrons that have higher aberration, but this does come at the cost of brightness. For my experiments, I stuck with the largest condenser aperture, which is $200\text{ µm}$, as I was able to attain good resolution with it and did not have highly beam-sensitive samples (e.g., biological material).

\textsuperscript{15} And geology\textsuperscript{16} Relatively speaking. TEMs are actually very complex instruments.
The first step of aligning the TEM for imaging is to align the height of the sample to Gaussian or eucentric focus, which is at the focal length of the objective lens. Practically, this is accomplished by adjusting the z-height of the sample polepiece until the sample itself appears to have minimum contrast (in phase-contrast imaging mode)\(^\text{17}\). When working with a thick sample that may not have an obvious sign that it’s at minimum contrast, another way to accomplish this is to converge the beam to crossover on a region of substrate on the sample. Doing this will create a convergent-beam electron diffraction pattern on the detector screen.\(^\text{17}\) To reach eucentric height, then simply adjust the z-height of the sample polepiece until the diffraction pattern completely contracts into the crossover spot\(^\text{16}\). A third method is to activate the TEM image wobbler and adjust the z-height of the sample polepiece until the image wobbling is minimized, however this method is not ideal for people who get dizzy easily.

The next step of the process, and one that is oft-repeated, is aligning the condenser aperture\(^\text{17}\). In order to perform the alignment, the beam is first brought to crossover, which is the smallest attainable spot, on an amorphous or absent part of the sample using the Brightness knob, and then centered on the phosphor screen using the Condenser Shift (or just “Shift”) controls. The beam is then spread using the Brightness knob turned clockwise until it nearly reaches the edges of the detector screen. If the beam does not expand symmetrically around the optical axis, the condenser aperture alignment is adjusted until it does. The beam is then brought to crossover again, re-centered if necessary, and then spread again to determine if the condenser aperture needs to be readjusted. If so, this process is repeated until this is no longer the case.

Next, the electron field emission gun needs to be aligned so that it too is centered on the optic axis\(^\text{17}\). For this, first increase the magnification to at least 100 kx and realign the condenser lens. Then, turn on the Anode Wobbler. Using the deflector/stigmator knobs (as opposed to the shift knobs), adjust the settings until the beam and the cross that form pulse symmetrically. After this, the condenser lens should once again be realigned, and I personally prefer to iterate through the gun deflector alignment again, just in case. The gun shift alignment is next in the process, which is performed by using Gun Align at TEM spot size 1 (which for modes other than diffraction is what I use to image) to center the beam at crossover, and then using the Shift knobs (Beam Align) setting.

\(^{17}\)Convergent-beam electron diffraction is an imaging method in and of itself, and one that can provide considerably more information about a sample than selected-area electron diffraction if one has the software to interpret the results, which I did not.
to center the beam at spot size 5. This process is also iterated until there is no change in position between spot size 1 and 5 at crossover. Once again, the condenser aperture will need to be realigned.

For two-dimensional materials on a flat substrate, sample tilt is not typically necessary for informative imaging—length of the c-axis is usually negligible compared to the surface area of the flakes, and height information can be more readily extracted from an AFM scan. Therefore, I typically skip the tilt-shift balance (or double tilt correction) step, which otherwise has the effect of minimizing how much the image of the sample moves when the sample is tilted in either the x or y directions. My SiNx substrates also do not fit in the double-tilt holder, so double-tilt experiments were impossible for Bi2Se3 experiments.

Therefore, the next two steps are to correct for condenser lens astigmatism and to perform the high voltage center alignment. Condenser astigmatism is image stretching or skewing along either or a combination of the x and y axes of the microscope due to irregularities in the condenser lens. The voltage center alignment, as the name implies, ensures that the highest potential for the accelerating voltage is centered on the optic axis. These factors are very important for ensuring the highest-resolution imaging, and along with the beam shift, are liable to change if the EMF cancelling system around the TEM drifts or picks up a fault\footnote{This is an irritatingly common occurrence, but typically either flipping the control switch for the EMF cancelling system to “Standby” and then back to “on” or a hard reset of the system by turning it off for one minute and then back on again will solve the problem for a time.} The standard operating procedure for the TEM lists two independent steps for these corrections\footnote{This is an irritatingly common occurrence, but typically either flipping the control switch for the EMF cancelling system to “Standby” and then back to “on” or a hard reset of the system by turning it off for one minute and then back on again will solve the problem for a time.}, but I personally strongly prefer the coma-free alignment technique taught to me by Douglas Yates\footnotemark[16]. In this method, the magnification is set to at least 100 kx, but for me typically the highest magnification I intend to image at, and the beam is brought to crossover on an unimportant region of the sample. At these magnifications, the beam and the caustic spot (the very bright spot in the center of the beam at crossover) are rounded triangular in shape, which is due to the shape of the FEG itself. When the astigmatism and voltage center are fully corrected, this triangle is equilateral in shape; the caustic spot is at the centroid of the beam; and bright lines will radiate from the caustic spot to the corners of the beam triangle in roughly the shape of the Mercedes-Benz® logo (see Fig. 2.3(a)). Astigmatism, shown in Fig. 2.3(b) will stretch the triangle and also split the spokes of the triangle, and voltage center misalignment (Fig. 2.3(c)) will make the caustic spot off-center in the beam, which stretches the triangle, rounds it, distorts the spokes, and makes the spokes fainter or causes them to disappear entirely. Once the user is familiar...
with the technique, it can be performed very rapidly and on the fly during imaging, and the shape of the beam and position of the caustic spot indicate the actual direction of misalignment, which makes it easier to determine how to correct the settings and when to stop, unlike with correcting the voltage center using the high tension wobbler, which is more of a “better or worse” comparison. After this step, the condenser lens should be realigned, and then this step should be repeated until no further adjustments to either the condenser alignment or the astigmatism and voltage center are needed.\(^\text{19}\)

![Figure 2.3: Schematic of the TEM beam at crossover at very high magnifications, showing (a) a well-aligned beam and caustic spot, (b) a beam with considerable condenser astigmatism, and (c) a beam with significant voltage center (or bright tilt) misalignment.](image)

The final step in the TEM alignment process is correcting for astigmatism in the objective lens. While objective lens astigmatism (OA) is more subtle to the eye than condenser lens astigmatism, it can still compromise high-resolution imaging and prevent image formation of atomic lattice. Due to its subtlety, the methods of spotting and fully correcting for objective astigmatism are all somewhat of an art form and require a trained eye and a relaxed mind, as well as imaging on an amorphous carbon or silicon nitride region of the substrate rather than the sample area of interest. Additionally, the sample needs to be verified to be at eucentric height/Gaussian focus, and the rest of the column must be well aligned, as other issues with the beam may look like OA, and correcting for it with a poorly-aligned column will simply introduce additional aberrations, especially after the prior issues are corrected. The first way to spot OA is in direct space, by looking at noise in the background for the image in Digital Micrograph. If the noise appears to travel primarily in one direction (e.g., left to right), I typically perform the entire column alignment up to this step twice before proceeding, a habit I picked up with the 2010F.
right) rather than radiating evenly outwards or having no perceivable source, OA is present and needs to be corrected\textsuperscript{16}. The second method involves using a live (continuous) FFT of the image, again, in Digital Micrograph\textsuperscript{17}. In this method, which is my preferred technique, the sample is brought to a slight underfocus, so that rings are visible in the FFT, and the objective stigmators are adjusted until the rings are round rather than elliptical. In this method, the direction of ellipticity (although in severe cases the FFT instead becomes an X shape) reveals the direction of astigmatism, so it is possible to determine which way to adjust the stigmators. This process too should be performed at the highest magnification to be imaged at, and it should be iterated with the condenser alignment and coma free alignment until all are acceptable. Digital Micrograph allows a reference circle to be drawn on the live FFT for a comparison, but because the long axis of the ellipse rotates \(90^\circ\) through focus, and because the long axis of the ellipse extends at conditions close to focus (though it is also fainter), I have rarely found this assistance necessary.

After the objective astigmatism is corrected, the TEM is ready to image the sample at high resolution. Image acquisition is typically performed either at a slight underfocus to improve contrast or at Gaussian focus, although there are many other focus conditions for more specialized applications. There are multiple ways to image and analyze samples within a TEM. A brief description of the methods I focused on follows.

One of the most basic forms of imaging within a TEM is called bright-field imaging. In this mode, an aperture is inserted after the objective lens in order to select only the fraction of the electron beam that passed through the sample without interacting strongly, which is known as the unscattered beam, or the (000) spot in diffraction mode\textsuperscript{16,18}. This mode tends to yield good contrast at lower magnifications and can reveal information about what areas of a sample do and don’t interact strongly with electrons. Electrons have the least chance of being strongly scattered when passing through thin areas of the sample and areas with lighter elements. Because it is the thinnest or most absent part of the area being imaged, the background appears bright, hence “bright-field.” The ray diagram for bright-field imaging is shown in Fig. 2.4(a).

If the objective aperture is instead moved off-axis and centered around a diffraction spot, the image formed on the detector will instead be bright in regions of the sample that strongly scatter the incident electron beam in that particular direction, and areas of the sample that do not scatter in that direction will be dark. Because the thin and amorphous substrate does not contribute to the
formed image, this method is known as “dark-field” TEM. Dark-field TEM’s main advantage is that defects and misaligned domains in crystals tend to contrast strongly with their host lattices, as the defects don’t scatter in the same way. Fig. 2.4(b) shows the ray diagram for this imaging method.

It is worth mentioning that while the 2010F was capable of the above two imaging modes, the F200 does not have a variable objective aperture, so it is not. How, then, does it form images? First, let us note that bright-field and dark-field TEM are not effective ways to image samples at atomic resolution. Regions that are similar across the sample will produce similar brightnesses, which means that at extremely high magnifications, there is essentially no contrast. But if the objective aperture passes more than one diffracted beam, as shown in Fig. 2.4(c), the result is an image that is composed of electrons that traveled along different paths through the TEM, and therefore have variable path length. This is precisely the setup that allows for interference conditions at the detector screen, which means that the different phases the electrons pick up during their journey through the TEM will be responsible for bright and dark areas of the sample as they interfere constructively or destructively. As one might guess, this mode is known as “phase contrast” imaging. Unlike bright and dark-field imaging, phase contrast is suitable for ultrahigh magnification imaging, as its contrast primarily
depends on scattering from individual atomic sites. This means that both the 2010F and the F200 microscopes, which as high-resolution TEMs (HR-TEMs) were built around this type of imaging, are able to resolve atomic lattice, and in the case of the F200, atomic columns and actual atoms. \(^{20}\) In order to actually attain sufficiently low aberration for this degree of magnification (typically 800 kx to 2 Mx), the convergence angle of the TEM is set to \(\alpha = 1\), which is a mode in which the beam impinges on the sample in as close to a parallel orientation as possible (that is, fully collimated rather than converging or diverging).

The final basic imaging mode in the TEM is known as diffraction imaging, which has its ray diagram outlined in Fig. 2.4(d). In this mode, rather than an objective aperture in the back focal plane of the objective lens excluding some of the more strongly-scattered beams, a selected area aperture is inserted in the image plane of the objective lens that excludes parts of the sample itself from contributing to the formed image. This allows the isolation of certain regions of the sample, such as a specific edge or domain, or the center of a flake rather than the surrounding substrate. From there, the imaging lens is relaxed so that its back focal plane rests at the focal plane of the projector lens instead of its image plane. Therefore, the image formed at the detector is of the spot (or ring, for polycrystalline and amorphous samples) pattern formed by Bragg reflection through the material, which is itself a way of physically performing a Fourier transform on the lattice.\(^ {16}\) From this image, the angles of the spots relative to each other and the ratios of their distances from the center (000) spot can be compared to tables of calculated diffraction patterns for specific crystal symmetries to be able to determine the symmetry of the crystal, the zone axis the crystal is being imaged from, and the Miller indices of each spot. From there, it is relatively straightforward to calculate the lattice parameters from measurements of each spot’s distance from the (000) spot.\(^ {19}\) To aid in this analysis, I have written programs for calculating the lattice parameters for close-packed hexagonal, tetragonal, and orthorhombic systems from indexed diffraction spots and spacings.

2.2.2. Substrate Choice

Many of my measurements in the TEM are performed with the sample resting atop an electron-transparent silicon nitride (SiNx) membranes, the fabrication of which is detailed above in Sec-

\(^ {20}\) The 2010F was allegedly also capable of imaging atomic columns, especially in annular dark-field STEM, but I certainly never reached that level with the one in the Singh Center. However, most of my imaging was done atop SiNx windows that were at least as thick as my samples and not suspended or on lacy carbon films, so my experience may not be indicative of its true prowess.
tion 2.1. SiN\textsubscript{x} membranes were the substrate of choice for many TEM experiments because they provide an excellent compromise between the need for a rigid and insulating material for stamping transfer and \textit{in situ} transport measurement and the need for minimal material in the vicinity of the sample in order to obtain superior contrast, clarity, and resolution during high-resolution TEM imaging. Additionally, while the nitride window does somewhat obscure lattice fringes and may introduce distortions into a direct-space image, it has a minimal effect on selected-area electron diffraction measurements. Instead of obscuring the lattice in reciprocal space, it merely adds minor amorphous background rings, as can be seen in Fig. 2.5. Additionally, SiN\textsubscript{x} contributes only silicon and nitrogen signals to EDS, and neither element is a component of any compound I studied. These windows, however, work best with thicker material samples—monolayers can be extremely difficult to find and image, especially for materials composed of low-Z elements such as vanadium. For FGT Lorentz TEM experiments, samples were transferred to SiN\textsubscript{x} membranes with FIB holes drilled in the center so that parts of the sample could be suspended during imaging.

![Figure 2.5](image.png)

**Figure 2.5:** (a) Selected area of amorphous silicon nitride for diffraction. (b) Diffraction pattern of SiN\textsubscript{x}. In addition to the central spot, inner and outer annuli can be seen in light gray.

2.2.3. \textit{Scanning TEM}

There is an additional TEM mode that I used extensively, which is known as scanning transmission electron microscopy, or STEM. In this mode, a much smaller condenser aperture is used, and rather than illuminating the sample with a wide, collimated beam, an extremely narrow probe that is brought to crossover on the sample is used. Proper imaging with this beam requires an adjustment to the z-height of the sample: rather than being at eucentric height, it needs to be at the point of infinite magnification—the sample should be one focal length from the upper objective, and one
focal length from the lower objective, so that parallel illumination incident on the upper objective is brought to focus (essentially crossover) on the sample, and when the beam exits the lower objective, it should be fully collimated.\textsuperscript{16} Fig. 2.6 shows a conceptual schematic of the ray diagram for a TEM operated in scanning mode, which illustrates the concept of infinite magnification nicely. In an ideal setup, each spot the probe beam illuminates is a zero-dimensional point. However, when the electrons scattered from that point reach the detectors, they have a finite width, and, even if the detector were infinitely far away, the beams radiating from each point would never converge to form an image. What is detected on the screen from this probe beam is known as a Ronchigram, and from a practical standpoint, it looks like a small circular puddle, and it is what is used to align the column in this mode.\textsuperscript{17} The first step is to align the gun by turning on the Anode Wobbler and using the gun defectors so that the Ronchigram pulses symmetrically about the center of either the viewscreen or the TEM mode imaging camera.\textsuperscript{21} Next, the condenser astigmatism is corrected. When condenser astigmatism is present, the Ronchigram looks like a cell in the process of mitosis, and when it is absent, the “puddle” looks quite smooth and relatively featureless, though there is often a brighter spot in the center. Going very slightly under and over focus can exaggerate the appearance of the astigmatism, so this can be a helpful trick for getting the best beam possible. After the Ronchigram is optimized, a condenser aperture is inserted and centered so that only the electrons forming the Ronchigram are allowed to illuminate the sample. An aperture the same size as or slightly larger than the probe beam will improve the brightness, and contrast, but this comes at the cost of resolution, as aberrations are present at the edges of the beam.

With the beam focused on to the sample in this way, it forms a convergent-beam electron diffraction pattern, as was briefly mentioned in Section 2.2.1. Imaging is performed by rastering the beam across the sample and essentially adding up contributions from all of the individual diffraction patterns formed. In the setups I used, two separate detectors form images from these contributions. The first is the bright-field (BF) detector, which is axial on the column, and it specifically images the electrons that did not interact with the sample or did so only to a small extent (essentially the (000) spot of the diffraction patterns). Like with TEM bright-field imaging, the areas of the sample with minimal amounts of material and lighter elements appear brighter, whereas heavier regions appear darker. The second detector, the annular dark field (ADF) detector is, as its name would imply

\textsuperscript{21}For the 2010F, this procedure was done on the viewscreen, but both Digital Micrograph and the control software are able to image the Ronchigram for the F200.

30
Figure 2.6: Diagram of a TEM operated in scanning mode with an EDS detector.
located in an annulus around the BF detector. Unlike with TEM dark-field imaging, however, the DF detector does not see contributions from only one diffraction spot. Instead, it detects many of the diffracted beams in a full circle all at once and adds them together. This allows for considerably more signal to the detector than in TEM dark-field.

STEM mode also allows for additional detectors to be used. For my experiments, I relied on an energy-dispersive x-ray spectroscopy (EDS) detector. EDS measures the characteristic x-rays from atoms with core-shell ionizations due to interaction with the probe beam, and therefore it can be used to identify the elements present in a sample with good accuracy, although it works best for heavier atoms and can run into difficulty when characteristic x-rays overlap\textsuperscript{22}. EDS is a semiquantitative method, as there are many complicating factors that can affect the accuracy of analysis, such as detector cross section and efficiency, sample density, secondary x-rays and x-rays produced by the column itself, emissions from the substrate and holder\textsuperscript{23}. The ability to manipulate the beam in STEM mode also allows for spectra collected at a single point on the sample, line scans across a region of interest, and even full 2D maps where each point has a collected spectrum of its own (though for time reasons, any map more than about 256 × 256 pixels has rather minimal individual spectra). For the 2010F, EDS analysis was performed using the EDAX TEAM software, and in the F200, EDS analysis was performed with Digital Micrograph.

2.2.4. Cryogenic TEM

The Drndić lab’s recently acquired Gatan Ultra-Low Temperature Double Tilt holder (ULTDT) extends the capabilities of the TEM down to at least 20 K, and potentially down to liquid helium temperatures. Because as of this writing only myself and one postdoc are trained on this equipment, the detailed standard operating procedure, as related to me by Joel Kasper during the training session\textsuperscript{20} is as follows:

At least one day before the TEM session, and preferably several, it is important to begin the dewar evacuation and bake-out process. Ideally, this is the time to insert the sample itself, so that it too may be cleaned of residuals. The vacuum used for the pre-pumping must be a dry pump; in our experiments, we used an Edwards NXDS6i scroll pump as backing for a turbomolecular pump. The

\textsuperscript{22}Vanadium and oxygen overlap, which made determining the degree of oxidation in the VSe\textsubscript{2} degradation experiments challenging.

\textsuperscript{23}The holder and copper grids for the VSe\textsubscript{2} specifically are the reason for the large Cu K\textsubscript{\alpha} peaks in my samples, and though they are not labeled, zinc and peaks from brass components are also present.
ULTDT holder is placed in the Singh Center pumping station and connected, albeit with valves closed. Next, the valves are sequentially opened down the length of the holder, saving the dewar for last and being sure to open very slowly so that the air does not shock the pump. The holder is allowed to evacuate until at least $10 \times 10^{-6}$ Torr, and then the bakeout process is started. To bake out the holder, its associated Gatan temperature controller is first connected, and then the “bakeout” option is selected from the options menu. During this program, the temperature controller will maintain the holder at 55°C for several hours. This allows adsorbed volatiles such as water molecules to desorb and be pumped away, which allows for better ultimate temperature and length of time the holder can remain cold.

On the day of the TEM session, the cooldown process is conceptually simple but physically awkward. Due to the necessity of handling two ends of a long, heavy transfer hose while simultaneously not breaking column vacuum, operation of the ULTDT holder is a two-person job. First, the liquid helium dewar is brought to the microscope room, the diaphragm pump for the dewar is turned on, and the ULTDT holder is disconnected from the vacuum, ensuring that the dewar is sealed off, the helium transfer valve is installed on the top of the dewar, and then the dewar should be carefully inserted into the TEM. It is necessary for a user to support the weight of the ULTDT holder during the insertion process, as its weight distribution may cause it to rotate or tip if not immobilized, which could dump the column vacuum and disable the TEM for at least several hours. The double-tilt cable and the heating and sensing cable are connected to the TEM and the Gatan temperature controller, respectively.

The first end of the transfer hose is then inserted into the large liquid helium dewar. This should be done while wearing a face shield and long cryo gloves for safety, and furthermore, it should be done slowly. An orange balloon is attached to one of the gas outlet ports in order to have an easy way to monitor boil-off from hose insertion. In general, this balloon should not get any larger than perhaps twice the size of the user’s head during the transfer process, and if it starts to get extremely large, the transfer rod should be pulled out several inches (but not entirely!), the non-emergency pressure relief valve opened\textsuperscript{24}, and the balloon squeezed until the rate of helium evaporation reduces. The orange balloon at the small end of acceptable levels of inflation is shown in Fig. 2.7(a). The user may then continue to proceed with insertion as before, but with more care. Boil-off can get overwhelming\textsuperscript{24}\textsuperscript{25}.

\textsuperscript{24}The emergency pressure relief valve should always be open, though under good circumstances it should not be venting.

33
quickly, and for safety it is extremely important that should the user flinch, the direction of the flinch is to pull back on the rod and not to drop it into the dewar entirely. The insertion valve can be tightened somewhat so that should the rod be dropped, it will not descend rapidly into the dewar.\footnote{Should the room-temperature rod be dropped into the large liquid helium dewar, attempt to pull it out. If the rod is stuck, evacuate the room quickly, close the door, and notify Doug Yates. You may wish to continue evacuating down the hall with haste. You are having a very bad day.}

Regardless, when the rod reaches the bottom of the dewar, the insertion valve can be tightened completely, and the users should wait for the transfer line to fill. The orange balloon may be squeezed to increase the pressure inside the dewar with warm helium to hasten the process somewhat. As the transfer line fills, it will audibly hiss: first as a pulsation, and then it will become continuous. Once the hiss is continuous and liquid helium begins to squirt out the far end of the transfer line, the hose should be inserted into the ULTDT dewar. Plumes of gaseous helium will vent from the release valve on the top, as is shown in Fig. 2.7(b, c). The dewar is full when instead of as a loose plume, the helium vents as a conical jet almost like the flame of a Bunsen burner followed by a plume. Some small droplets of liquid helium may also fly out of the venting valve at this stage of the process. At this point, the transfer hose should be carefully removed from the ULTDT dewar, a heat gun used to defrost the filling valve (as you can see in Fig. 2.7(c), it gets very frosty indeed), and the filling valve replaced with the pressure regulator. Fig. 2.7(d) shows an \textit{ad hoc} pressure regulator made by cutting a slit in some silicone tubing during the training session, but the actual part arrived several days after the training session, so this solution is no longer necessary. The pressure regulator should be screwed down fairly tightly\footnote{As always, do not overtighten the fittings.}, as failing to do this can result in the part flying off the dewar.
without warning, and it may hit the user in the head or face. This surprise venting process will also release a considerable quantity of helium from the dewar and dramatically increase the temperature. Simultaneously, the transfer hose should also be removed from the large liquid helium dewar and the valve closed. Once they are warm, all parts that were in contact with cryogenics should be wiped down with a lint-free absorbent towlette such as a KimWipe™ to remove condensed water. Never reinsert the transfer hose without drying the rod, as water ice may clog the line.

Now, the vacuum line may be attached to the back of the dewar and the needle valve opened to increase the helium flow rate. As the holder cools, it is recommended to have a flow rate of about 3 reading on the float valve until 30 K, after which the flow should be reduced to around 0.3. During imaging, the flow rate can be adjusted as necessary to balance out with the set point of the Gatan temperature controller. The higher the flow rate (the more open the float valve), the colder the temperature will be.

Once the sample has reached the desired temperature, TEM alignment and imaging can proceed as usual. If images are to be taken at multiple temperatures, the user should bear in mind that there is fairly extreme sample drift as the temperature changes due to thermal expansion, so if the user wishes to maintain focus on a specific feature, this too is a two-person endeavor. The user most familiar with TEM operation should remain at the controls with a good eye and a quick hand on the stage positioner trackball while the other user adjusts the temperature setpoint and the flow controller.

Throughout the course of our experiments, we found that the lowest temperature we could stabilize to was approximately 20 K, though we expect this is due to not being able to pump out the dewar jacket to ultrahigh vacuum ($1 \times 10^{-7}$ Torr or better) with the current pumping setup. Fig. 2.8 shows sample TEM images of VSe$_2$ taken at 1 Mx at various temperatures during a controlled heating process. Fig. 2.8(e) shows a typical heating curve for the sample with respect to time and imaging points, although the linear spline between the points is used as a visual aid rather than an indicator of a linear heating rate.
2.2.5. Lorentz TEM

Another method I used in the TEM is known as Lorentz TEM. In this mode, the objective lens is turned off, and the objective mini lens is used to focus the sample\textsuperscript{16}. In the F200, this corresponds to Low-Mag mode, but in other TEMs, there is a dedicated Lorentz lens that allows for higher magnifications. The benefit of operating the TEM in this regime is that for ferromagnetic materials, lateral magnetic domains in the sample can be imaged directly.\textsuperscript{16} Systems that are able to go to higher magnifications than the F200 in Lorentz mode are also able to image skyrmions\textsuperscript{21}, although such spin textures are too small to be imaged in Low-Mag mode in the F200. Regardless, we used samples of iron germanium telluride (Fe\textsubscript{3}GeTe\textsubscript{2}, or FGT) from Deep Jariwala’s lab to develop a procedure for cryo-Lorentz TEM in the F200.

As previously mentioned, in order to avoid magnetizing the sample with the objective lens, the objective lens itself should be turned off, and the objective mini-lens used to focus on the sample.
In addition, the lenses themselves should be degaussed before sample insertion, which is available in the free lens control settings. Degaussing the lenses brings the residual field at the sample as close to 0 as possible, which is useful if one does not want the TEM coils to magnetize the sample. Once the lenses are degaussed, the transfer arm can be inserted into the microscope, and the column aligned in Low-Mag mode. Because the objective lens is off, objective astigmatism does not need to be corrected.

Examples of images taken during cryo-Lorentz TEM of iron germanium telluride (Fe$_3$GeTe$_2$, FGT) are shown in Fig. 2.9. Fig. 2.9(a) shows an image of eye-like features that form due to converging magnetic domains. Fig. 2.9(b) shows an almost trilobite-shaped pattern of magnetic domains located in the FGT sample. This pattern was not beam-sensitive, but it did change slightly when the lenses were degaussed a second time as a test. Fig. 2.9(c), on the other hand, shows some more typically-found magnetic stripe domains in FGT.

Lorentz TEM images are interpreted by taking a through-focus series on a specific set of magnetic features and comparing the changes in Fresnel fringes.$^{16}$ Fig. 2.9(d-f) show FGT magnetic stripe domains under, at, and over focus, respectively.

2.2.6. Unconventional TEM Stabilization Techniques

Before the upgrade from the JEOL 2010F to the JEOL F200, TEM experiments often suffered from column vibrational issues that degraded the quality of images and the ultimate attainable resolution. To combat this issue, a procedure was developed in which heavy textbooks, equipment manuals, and binders were stacked atop both the column and the shielding box for the sample holder. The extra weight on the column was found to assist in damping vibrations and allowed for considerably improved measurements.$^{22}$ In addition, delicate techniques such as in situ nanosculpting of Bi$_2$Se$_3$ were performed at night, when vehicle traffic was lighter and when both the Market-Frankford subway line and the nearby trolley lines ran less frequently.

2.2.7. Raman Spectroscopy

Raman spectroscopy is a spectroscopy technique in which (typically) visible or near-infrared light is focused on a material and the reflected light analyzed. During the reflection process, photons are absorbed by the electrons in the material and then re-emitted at or nearly at the same frequency
Figure 2.9: Lorentz TEM images of FGT at low temperature. (a) Image of converging magnetic domains in the sample. These features are beam-sensitive and seem to track the center of the beam when the stage is moved, which can be lightly unsettling for the user. (b) Highly aesthetic trilobite-shaped magnetic domains. (c) More standard stripe domains appearing in the same sample. (d) Through-focus series of stripe domains at significant underfocus. (e) Through-focus series of stripe domains at Gaussian focus. (f) Through-focus series of stripe domains at significant overfocus.

as the electrons return to their ground state. The “nearly at the same frequency” photons are what Raman spectroscopy examines, as these small energy shifts in the reflected light are due to either losses (Stokes shift) or gains (anti-Stokes shift) as a result of phononic excitations within the material. In Stokes shift, after an electron is excited by a laser, it decays vibrationally to a lower energy before re-emitting a photon. In anti-Stokes shift, the electron begins in a vibrationally excited state when it is excited by the laser, so when it drops back to its ground state, the photon energy is slightly greater than the excitation energy. The phonon spectra of materials strongly depend on both the individual bond strengths—which may be likened to spring constants—and the symmetries present in the material and its surroundings, which determine the types of allowed vibrations. Other material conditions such as stress, strain, defects, and dopants all can contribute to shifts in the Raman spectra of materials, which makes Raman spectroscopy a powerful tool for both material
identification and probing the details of a material’s quality and environmental interactions. In 2D materials especially, substrate effects can be extremely relevant, in particular to the out-of-plane modes\textsuperscript{23}.

For Bi\textsubscript{2}Se\textsubscript{3} experiments performed at the University of Pennsylvania, the Nano/Bio Interface Center’s (NBIC) Scanning and Local Probe facility’s confocal Raman-NSOM equipment was used with the 491 nm and ultranarrow notch filter I selected and which the Drndić lab acquired for the setup, as the lasers and filters available for the instrument at the time had a cutoff that obscured Bi\textsubscript{2}Se\textsubscript{3} peaks. Raman spectroscopy on VSe\textsubscript{2} was performed in the NBIC Scanning and Local Probe facility’s Horiba Raman spectrometer at a wavelength of 785 nm.

2.2.8. Atomic Force Microscopy

An atomic force microscope, or AFM, is a machine that, put very simply, pokes things to see how tall they are.

An AFM is composed of a sample stage, a tip carrier with piezoelectrics mounted in it, a laser, some mirrors and lenses, a photodetector, and machinery to raster either the tip carrier or the sample stage, control electronics, and a lock-in amplifier. To use an AFM, it is necessary to load an AFM tip into the tip carrier. An AFM tip is a small, correctly-shaped\textsuperscript{27} piece of silicon with a very small cantilever (a few microns long and a micron or two wide) with a reflective coating that has at its end an extremely small and sharp downward-facing tip (radius on the order of nanometers). The cantilever has a well-defined spring constant. Once the AFM tip is loaded into the tip carrier, the laser, mirror, and photodetector should be aligned such that the laser bounces off the back of the cantilever and is then reflected by the mirror into the photodetector. The process for aligning the laser onto the AFM cantilever in a Bruker Multimode 8 is diagrammed in Fig. 2.10\textsuperscript{28}. In order to perform the alignment, the scan head with the loaded tip should be held over a white sheet of paper such that the reflection of the laser is clearly visible. The laser is first brought to the “top” of the alignment area, then moved to the right so that it is near the edge of the AFM tip body. It should then be adjusted downwards until the laser is just starting to be blocked by the silicon chip. The user should then count the number of turns of the y adjustment knob it takes to bring the laser just to

\textsuperscript{27} It must fit snugly into the tip carrier

\textsuperscript{28} The alignment procedure for the Bruker Dimension Icon can be found in the NBIC’s standard operating procedure for the instrument.
the point where it starts to become visible on the far side of the AFM tip body. The y adjustment knob should then be turned in the other direction for half the number of turns it took to reach the far end of the chip. Finally, the x adjustment knob should be turned so that the laser moves left along the cantilever until the signal is maximized. Slight y adjustments may be necessary to center the laser on the cantilever to further improve the signal. Without considering the signal, the laser can be determined to be in a near-optimal position when the laser is obscured but any slight y adjustment or any leftward x adjustment reveals it. Checking this condition is important because other reflective surfaces in the housing can appear to give a very high signal, but they will of course not vary as the tip interacts with the sample, which can lead to the tip crashing into the surface and breaking. Once optimized, the laser signal should then be “balanced” on the photodetector such that the signal is roughly centered rather than dominant in any one quadrant. Additionally, the specific AFM tip model should be loaded into the control software so that the instrument is aware of the spring constant of the cantilever. The next steps depend on the operation mode of the AFM, but the basic idea for all modes I used was that the AFM tip is oscillated by the piezoelectrics in the tip carrier while very close to the sample. The tip makes gentle contact with it or interacts via long-range forces, which perturbs the tip oscillations or causes deflection. The change in the cantilever’s behavior is picked up by the photodetector; the signal is amplified by the lock-in; and then analysis is performed by the control software to extract a height profile, an error measurement, and in some cases a phase profile.

![Diagram](image_url)

Figure 2.10: Conceptual diagram for aligning the laser for the Multi Mode 8-HR AFM.

The typical operating mode for my Bi$_2$Se$_3$ AFM measurements was “tapping mode.” In this mode, the cantilever is oscillated at about 95% of its resonant frequency in air. During the tuning process,
which finds the optimal drive frequency to oscillate the cantilever, a measurement of the “free amplitu-
dete,” or amplitude in the absence of any external forces, is also taken. During AFM measurements, 
an amplitude setpoint, which is some fraction of the free amplitude, is chosen, and this is the ampli-
tude of oscillation that the AFM will attempt to maintain. The presence of force gradients acting 
on the tip will change the effective spring constant $k_{\text{eff}}$, which in turn detunes the cantilever and 
changes its oscillation amplitude. Repulsive force gradients have the effect of increasing $k_{\text{eff}}$, and 
attractive force gradients decrease $k_{\text{eff}}$. Because the cantilever is so close to its resonance peak, the 
amplitude changes that result from this detuning are considerably larger than the height of the fea-
ture causing them, which makes the variation easier to detect. The AFM then adjusts the height of 
the scanner in order recover the amplitude setpoint. This adjustment is then analyzed to determine 
the height of the feature. In addition, interactions with different surfaces cause different amounts of 
phase shift for the tip oscillations, which can also be used to determine information about different 
materials present in a sample. In tapping mode, the cantilever needs to be fairly stiff, otherwise it 
can get stuck to the surface of the sample\textsuperscript{24}. The tips used for Bi$_2$Se$_3$ measurements were the bulk 
tips available for users of the NBIC Bruker Dimension Icon\textsuperscript{®}.

Even in the absence of measurements, the resonant frequency can be affected by external factors 
that can negatively affect the resolution and contrast in unexpected ways, so it is important for the 
tip to be clean and seated properly in the tip holder. During the tuning process, abnormalities will 
appear as double or side peaks in the resonance. If these features are present, the tip carrier should 
be removed from the AFM and the tip adjusted so that it does not touch the back or side walls 
of its housing. If several attempts to fix the position of the AFM tip do not resolve the issue, the 
cantilever is likely damaged or contaminated and should be replaced.

Once the cantilever is properly aligned, it is best to begin with a low-resolution scan in order to find 
an area of interest and begin optimizing the individual parameters such as the setpoint amplitude 
ratio and the PID settings, before moving to a higher-resolution scan and then decreasing the 
scan speed until acceptable resolution is obtained. Optimizing the scan parameters is more of an 
art than a science, so I cannot report a full procedure for it, but in general it is best to use the 
highest setpoint amplitude possible that still allows for tip contact and tracking with the sample and 
produces appropriate edges\textsuperscript{29}, as a low amplitude setpoint causes firmer contact with the surface

\textsuperscript{29}AFMs inherently run into difficulties with vertical edges and tend to overshoot them slightly. This effect is a result of the AFM tip oscillating vertically and therefore not being able to track vertical surfaces and can be mitigated, but
and will wear the AFM tip down more quickly, leading to a need for more frequent replacements and therefore significantly higher operating expenses. Too low of an amplitude setpoint can also increase the noise in the scan. Once basic tracking is attained, the next parameter to modify is the integral gain in the PID settings. This parameter affects how quickly the system responds to changes in order to maintain the amplitude setpoint. In general, increasing this parameter tends to improve tracking up to a point, but if it is increased too far, it leads to significant noise as the system begins to overshoot the corrections. The next setting to change is the proportional gain, which also affects the response of the system to changes in tip-sample forces, but less so than the integral gain. In general, it should be around $2\times$ the integral gain. A slower scan is always a better scan, but this should be the last parameter modified for best user efficiency\textsuperscript{24}.

While the Dimension Icon\textsuperscript{®} is an excellent AFM, as part of a user facility it is subject to the wear and tear of many operators with varying degrees of skill, and as a result, I found that the scan head became increasingly loose and wobbly over the span of several years. “Loose and wobbly” is not an AFM condition conducive to precise, low-noise, and delicate measurements with sub-nanometer accuracy, particularly for the non-contact method of magnetic force microscopy (MFM) I needed to perform as part of my VSe$_2$ experiments. This condition, along with continuing expenses from equipment reservations, drove the Drndić lab’s decision to acquire a new AFM specifically for the lab. I personally researched purchasing options and was the primary point of contact for acquisition, installation, and training. I selected a Bruker MultiMode\textsuperscript{®} 8-HR: its small footprint made it easy to install in the Drndić lab AFM room\textsuperscript{30}; its price fit the budget; and its capabilities are modular, which allows for easy future upgrades should future students wish to perform additional measurement types. Currently, the AFM can perform tapping mode in air, traditional contact and non-contact AFM, surface potential microscopy, MFM, electric force microscopy (EFM), torsional resonance AFM (TR-AFM), and Bruker’s proprietary PeakForce Tapping\textsuperscript{®}, ScanAsyst\textsuperscript{®}, and ScanAsyst-HR modes\textsuperscript{®}. All three of Bruker’s proprietary modes are based upon collecting force-distance curves at each pixel using pN forces, and analyzing these to get topography data. The cantilevers are not operated near resonance. Instead, they are driven at 2 kHz, 4 kHz or 8 kHz, which, when combined with the scan rate parameter, can allow for multiple force-distance curves to be averaged for each not removed, by decreasing the amplitude setpoint and by slowing the scan down.

\textsuperscript{30}The Drndić lab also has a Veeco environmental AFM capable of performing AFM, MFM, and EFM measurements under vacuum and at cryogenic temperatures, but unfortunately its control computer has ceased to function, and Bruker no longer maintains Veeco equipment. The room itself is no more than 5 m$^2$, so space is at a premium.
The ScanAsyst® and ScanAsyst-HR® modes differ in that they are self-optimizing: the user typically does not need to adjust any settings, as the software performs the adjustments itself based on the shape of the force-distance curves\(^{24}\). This is a considerable time-saver and is the reason why topography measurements of VSe\(_2\) were typically performed in ScanAsyst-HR® mode (which is capable of operating at 8 kHz). For measurements in ScanAsyst® mode, Bruker’s ScanAsyst-Air tips were used, and for measurements in ScanAsyst-HR® mode, Bruker’s ScanAsyst-Air-HR tips were used.

Magnetic force microscopy is a modification to tapping mode that allows for the sensing of surface magnetic fields from a sample. MFM is performed with a special type of AFM tip that has a magnetic reflective backing instead of a normal one, and the tip itself is also magnetized before use. During the scan, two passes are made across a given scan line instead of one. The first pass is a normal tapping mode pass and records the topography of the sample. The second pass, on the other hand, takes place a defined height above the sample—for my experiments typically 10 nm to 60 nm—so that only the long-range magnetic forces interact meaningfully with the tip. The magnetic force is quite weak, so the interaction primarily appears in the phase rather than in deviations from the amplitude setpoint. In addition, this method is purely semi-quantitative for several reasons. First, the details of the interaction depend strongly on unknown quantities such as the exact shape of the AFM tip and the exact magnetization of the tip. Second, the surface fields of the sample do not necessarily correspond to its overall bulk magnetization, although this effect is minimized in 2D materials, as the bulk simply does not exist apart from the surface. And third, the long-range nature of magnetic interactions means that the point directly beneath the AFM tip is not the only one to contribute meaningfully to its behavior. These long-range interactions also mean that MFM has a lower ultimate resolution than topographical AFM measurements. Regardless, it is a very useful technique for assessing whether a sample interacts magnetically and comparing the degree of response for different regions within a single scan (e.g., comparing monolayer and multilayer regions within VSe\(_2\)). In theory, MFM scans should take about twice as long as basic tapping mode scans, but in practice they take significantly longer. This is because the MFM scans typically need to be performed more slowly than normal scans for improved signal-to-noise ratio and to avoid the tip crashing into any vertical features during the lifted pass. The tip colliding with features during the lifted pass leads to spurious large spikes in the data that can be exceptionally tedious to remove and may also contribute to rapid tip wear. For VSe\(_2\) MFM experiments, Bruker’s MESP-V2 probes...
were used.

Because VSe$_2$ is a lateral ferromagnet, I have also developed an entirely new AFM technique, which I call torsional resonance magnetic force microscopy, or TR-MFM. Torsional resonance mode is a somewhat obscure AFM technique in which piezos on either side of the AFM probe excite the cantilever into a torsional, or twisting, mode, so that the tip itself sweeps out an arc as it passes over the sample. The cantilever is considerably stiffer in this direction, so the driving frequency is considerably higher. The mode itself is highly sensitive to lateral forces and therefore is most frequently used by tribologists. My idea was to combine this torsional oscillation with the lift pass of MFM so that instead of lateral frictional forces, lateral magnetic forces from VSe$_2$ would interact with the tip. As will be shown in Chapter 4, I was successful in performing the technique, but I report more details about it here. The probe used should be a standard MFM probe (MESP-V2 in my experiments). In order to set the mode up, the torsional probe carrier should be used, and the torsional mode selected in the “Experiments” menu of the software. Two tunings must be performed: the normal tapping mode tuning and the torsional resonance tuning. The torsional resonance frequency and the quality of the peak is even more sensitive to the position of the probe within the holder, so it is essential that it is seated properly. The first pass of each measurement line should be set up as a normal tapping mode pass, as TR-AFM can cause extremely rapid tip wear on any sample that is not perfectly smooth. The second pass should be set up to be performed with torsional oscillation and at a lift height of 15 nm to 50 nm. Because of the trajectory of the tip, the probe is even more sensitive to crashing into sharp vertical features, and therefore a slightly higher baseline lift height (and lower scan speed) should be used. However, this mode also probes a weaker interaction, so typically a lower height is also necessary to actually be able to image the sample. For this mode, it is strongly recommended to first optimize the topographical scan parameters and find as featureless an area as possible on the sample before enabling the lift mode. Even with these consideration, the mode is quite finicky, so operator patience during optimization, a supply of fresh tips in case the one in use breaks or wears on a sudden feature, and, whenever feasible, snacks are all keys to imaging success.
2.3. Probe Station

One of the main equipment projects I’ve worked on during my time at the Drndić lab has been overseeing the installation, maintenance, and training for the ARS closed-cycle liquid helium cryogenic probe station the lab purchased in 2017 and received in 2019. The platform itself has five electrical and one optical probe for transport and laser experiments, two cryocoolers for independent magnet and stage temperature control, and a 6 T superconducting magnet capable of producing 3 T at the height of the sample stage (which is not located in the center of the solenoid). The probe station uses 20 mil diameter long beryllium copper probe tips, and I’ve found that the model number 7H-45-LONG tips from Micromanipulator work best, as both the length and the 45° bend allow for greater probe reach and a superior contact angle with the sample. Shorter probes tend to encounter the issue of the probe arm bottoming out against the radiation shield before the tip can make contact with the sample if the sample itself is not positioned very precisely.

In addition to overseeing the instrument itself, I have written several Python programs for operating the various electronics attached to the probe station, including the Keithley 6221/2182A stack, the Keithley 2400 Source Meter, the LakeShore 336 Temperature Controller, and the AMI 431 Magnet Power Supply. Code for these projects is available via my GitHub page (https://github.com/safrie). Included with the Probe-Station repository is a configuration file that lists, among other parameters, the safe operating limits of the magnet.

2.3.1. Basic Operation

The standard operating procedure for the probe station is as follows:

To perform sample exchange, the probe station must be at room temperature to prevent water from condensing inside the system. When the temperature gauges read approximately 290 K and a sample is ready to go into the station, ensure that the compressors are turned off, that the vacuum pump and the He leak detector are either off or that the valves leading to them are closed, and open both valves leading to the nitrogen purge gas cylinder. Nitrogen should remain flowing during the sample exchange so that the system stays as dry as possible. If the system was under vacuum, the

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31 However, AMI has since published their own software that I’ve decided to use instead because it has been thoroughly debugged on an instrument other than mine and is therefore safer to use with the expensive equipment.

32 Condensed water will make the station take considerably longer to pump down, and water ice is in general very bad for cryogenic systems.
nitrogen will eventually break the seal and allow for the lid to be removed. Once the lid is off, place the rubber protector over the lid of the radiation shield so that the holes line up with the location of the nuts and use a socket wrench to remove the brass nuts. Once the nuts are removed, remove the radiation shield lid and fully retract the probes. If necessary for working space, remove the probes by loosening the probe arm set screws and pulling gently downwards with a pair of tweezers.

If the sample is to be gated, first mount the sapphire coverslip by dabbing a small amount of Apiezon N cryogenic grease to the back and then placing it on the sample stage. Ensure that the grease evenly coats the bottom of the coverslip in a thin layer by pushing it back and forth across the stage with tweezers, ending with it centered. Then, use the wooden end of a cotton swab to dab a very small amount of Apiezon N grease to the back of the sample and use tweezers to mount it atop the sapphire coverslip. Again, use tweezers to push it back and forth so that only a thin, even layer is between it and the coverslip. Thick or uneven grease will cause bad thermal contact. If necessary, re-install the probe tips by inserting them into the probe arms from below and ensure that they are capable of making contact with all relevant sample leads before proceeding: they cannot be adjusted while the system is closed, and both cooling down and warming up the station are overnight processes.

Clean the radiation shield lid with isopropanol and a lint-free wipe and then replace it on top of the can. Once again place the rubber protector over the lid, place the nuts, and gently tighten. The nuts should be worked on in a cross-tightening pattern and should not be overtightened. Then, clean the lid o-ring with isopropanol and then very lightly re-grease with standard silicone vacuum grease. After replacing the o-ring, clean the underside of the lid with isopropanol and then place on top of the station. Turn off the nitrogen flow.

At this point, if the turbomolecular (turbo) pump is turned off, turn it on, and forcefully hold the lid down as it starts to spin up. If the turbo pump is merely valved off, have a friend forcefully hold down the lid while you very slightly crack the valve. The pressure registered at the Pirani gauge will increase, then decrease. Once it stabilizes or is decreasing steadily, it is safe to crack the valve a little bit more while the friend continues to hold down the lid. Once the pressure is at least \(0.1 \times 10^{-3}\) Torr, the lid will probably be seated snugly, and external pressure can be released. Be aware for any whistling noises coming from the lid, as this indicates an air leak. In this case, if

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33This is so that the nuts do not fall into the can, as they are extremely difficult to retrieve and can cause thermal shorts, which adversely affect base temperature.
pushing down harder does not work, the vacuum should be turned off or valved off and the o-ring cleaned and re-greased. Once the lid is seated, if the valve to the probe station is not completely open, it can be slowly opened without shocking the turbo pump. If the Edwards turbo pump is used rather than an Alcatel pump, the backing rotary vane pump may produce a foul odor and unpleasant noises on startup, but these will quickly dissipate.

At this point, the fill level of the water-water heat exchanger should be checked, and if it is not full, it should be topped off. Corrosion inhibitor should be used in the process water loop, otherwise the internals of the exchanger will rust. This information is not communicated in the user manual for the heat exchanger, so mark it well. Once the exchanger is full, all four inlet and outlet tubes in the reservoir will be fully covered, and it may be turned on. Ensure that it remains on after engaging the momentary switch, and then wait for the temperature gauge on the process loop (black insulation) to match the temperature on the input side of the facility chilled water (white insulation). The facility water temperature is seasonally variable due to thermodynamic factors during distribution from the cooling plant, so the helium compressors will operate more efficiently in the winter.

When the process chilled water is ready and the vacuum gauge reads under $0.1 \text{ mTorr}$, the helium compressors may be started. This is a good point to check the leak detector, as a leak in the cryocoolers may make itself apparent once the system is pressurized. Passively monitor the system for at least an hour after the compressors are turned on and check the process water temperature to ensure that the compressors do not overheat, as they will automatically shut off. If they do shut off due to overtemperature, the water chiller may need a water change, the water filter may need to be changed, or the water chiller may need to be serviced.

Cover the probe station window so that light cannot enter the system and allow the system to cool down for at least 10 hours before beginning measurement. Before attempting to energize the magnet, ensure that the temperatures for the magnet top and plate are both below 5K. 5K is somewhat below the transition temperature of the magnet itself, which is somewhere between 7 K to 10 K depending on its current. This margin exists as a safety measure: quenches can severely damage the system, in particular some difficult-to-obtain diodes, so an actual quench can take the instrument offline for some time. Even with the magnet below its quench temperature, various

34 Leaks may also open up only at low temperature, so be sure to check again every so often.
35 I have not quenched the magnet, but ARS has, and it delayed delivery by several months.
factors can lead to temperature spikes, and a few degrees of wiggle room can help prevent damage. Additionally, before attempting to energize the magnet, ensure that the resistance across the HTS leads going to the magnet is between 0 Ω to 5 Ω, to verify that they are, in fact, superconducting. At room temperature, these leads have a resistance of approximately 3 kΩ. As a final safety step, ensure that there are no ferrous materials such as the socket wrench used to manipulate the radiation shield nuts within the 5-gauss line and that people with pacemakers, phones, computers, student IDs, and credit cards are all outside the 5-gauss line as well.

When energizing the magnet, first turn on the magnet power supply programmer and wait for it to complete the startup process before turning on the magnet power supply. Similarly, when turning off the magnet, first ensure that the current is zero, then turn off the magnet power supply, and finally turn off the power supply programmer. The parameters for energizing the magnet are as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Current</td>
<td>26.3 A</td>
</tr>
<tr>
<td>Maximum Magnetic Field</td>
<td>3.0 T</td>
</tr>
<tr>
<td>Maximum Ramp Rate</td>
<td>0.0254 A/s</td>
</tr>
<tr>
<td>Voltage Limit</td>
<td>3.0 V</td>
</tr>
<tr>
<td>Stability</td>
<td>36.5 %</td>
</tr>
<tr>
<td>Max Temperature While Energizing</td>
<td>5.9 K</td>
</tr>
<tr>
<td>Max Stage Temperature at 3T</td>
<td>225 K</td>
</tr>
</tbody>
</table>

In general, the magnet power supply should be turned off while editing the magnet power supply programmer settings to avoid accidentally applying unwanted settings.

When operating the LakeShore 336 temperature controller, the typical PID settings are $P = 50$, $I = 20$, and $D = 0$, but $P = 45$, $I = 10$ to 15, and $D = 0$ may also be useful. As with the AFM, decreasing the proportional and integral factors decreases overshoot, and the derivative factor is not typically important for our purposes. Be sure to monitor the magnet plate and top temperature while changing either the stage temperature or the magnet current to avoid a quench. It is possible for the magnet to quench while the system is decreasing the current to zero, so ensure all heaters are turned off and the magnet is at base temperature before doing so. If the temperature starts to spike near 5.9 K, reduce the ramp rate in order to reduce inductive effects.

When warming the probe station, ensure that the magnet power supply and programmer are turned off, and then turn off the compressors and the cooling water. Allow the probe station to warm
naturally for 24 h to 48 h, and if it is still too cold, the stage and radiation shield heaters can be set to 300 K and maximum output power. When the probe station is warm, follow the instructions at the beginning of this section for breaking vacuum and sample exchange. Isopropyl alcohol is insufficient for removing Apiezon N grease from the sample. Instead, the sample must be washed in an aromatic hydrocarbon solvent such as toluene, xylene, or limonene\textsuperscript{36}.

2.3.2. Maintenance and Troubleshooting

In general operation, the probe station compressors need to have their absorbers changed and the cold heads need their seals changed approximately every 12 to 13 thousand hours, and ARS should be contacted for information on ordering these parts. The oil for the rotary vane backing pump should be changed monthly with regular use, and the leak detector should be allowed to perform internal calibration regularly. If for any reason the leads for the magnet power supply are disconnected from the magnet, the terminals for the magnet should be cleaned with DeoxIt or another electronics-safe copper cleaner before the leads are reconnected\textsuperscript{37}

There is a white box between the heater outputs of the LakeShore 336 temperature controller and the heater inputs for the probe station. This box contains diode-LC filters I built for the heater in order to clean the output signal, as otherwise it produces unacceptable levels of electromagnetic interference during semiconductor measurements at any heater setting other than “off.” The conditioner itself includes German WWII-era radio capacitors, which are difficult to source, so I suggest this conditioner be handled with care.

In the event that the leak detector detects a helium leak, the following procedure should be performed in order to request maintenance from ARS:

1. Note the base temperature of the system and the vacuum pressure.

2. Note the level of helium detected with the compressors running and the system at base temperature. Take a picture of the flow rate graph.

3. Turn off compressor 2, allow several minutes for the helium reading on the leak detector to stabilize, and then note the helium level with only compressor 1 running. Take a picture of

\textsuperscript{36}I recommend limonene because of its low toxicity and pleasant odor.

\textsuperscript{37}Absolutely no vinegar/salt solution!
the flow rate graph, as it may show a sudden spike.

4. Turn compressor 2 back on and allow the system to return to base temperature.

5. Turn off compressor 1, allow several minutes for the helium reading to stabilize, and then note the helium level with only compressor 2 running. Take a picture of the flow rate graph, as it may show a sudden spike.

6. Turn off compressor 2 and allow the system to warm to room temperature.

7. At room temperature with the system still under vacuum, note the level of helium detected by the leak detector.

8. Verify that the leak is a helium leak by changing the settings first to detect $^3$He and then to detect H$_2$. These readings should be at or very nearly zero. Change the leak detector back to detecting $^4$He.

9. Assuming that the previous step did indeed verify a $^4$He leak, turn on compressor 1 and again note the level of helium detected over the span of a few minutes. Again take a picture of the graph to demonstrate any sudden spikes. Turn off compressor 1.

10. Allow the system several minutes to stabilize, and then repeat the above step with compressor 2.

11. Note the helium pressure in each compressor while turned on and while turned off.

12. Gather this information in an email and send it to ARS. If any spikes appeared in the graphs, they will identify the leaking cryocooler. Be prepared to perform this test a second time to verify its results before they agree to service the cryocoolers.

Fig. 2.11 provides a basic summary of the most serious of the many issues I faced while attempting to bring the probe station up to and maintain its specified capabilities after installation. In short, the water-water heat exchanger failed twice and needed professional maintenance; the heater conditioner needed to have its parts acquired and then assembled so that measurements of semiconductor systems at the promised variable temperatures were possible; the filter canister on the process water loop was unable to perform at the specified pressures, sprung a massive leak, and needed to be replaced; the 20-year-old Alcatel turbo pumps reached the maintenance interval at which their bearings needed to
be replaced, which I performed, and then had their power supply and controllers fail, which needed professional service; each cryocooler failed on two separate occasions, the first of which occurred together during installation and was easily fixed, and the second of which were each one developing a leak, which required ARS to return the entire probe station to their facility for at least a month for replacement on two separate but sequential occasions. The only current outstanding issue with the station to my knowledge is that after the cryocooler replacement, the cryocooler vibrations appear to have increased to the point that maintaining electrical contact between the probes and the sample is challenging. Currently, several textbooks, a lead brick, and several cases of optics screws are being used to minimize the pulse tube vibrations, similar to the technique outlined in Section 2.2.6 for the TEM, but as these vibrations are considerably more powerful, the efficacy of the technique is reduced. In addition, the optics screws are ferrous and therefore obviously cannot be used while the magnet is energized. The long 45° probes may also be able to establish more secure contact than straight probes due to their more aggressive attack angle. Except where specifically mentioned, these failures took place sequentially rather than in parallel\textsuperscript{38}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.11.png}
\caption{A graphical summary of the many equipment challenges with probe station operation.}
\end{figure}

\textsuperscript{38}This had the effect of completely maximizing instrument downtime, to my dismay.
CHAPTER 3 : Bismuth Selenide Experiments

3.1. Introduction

3.2. Background on Bismuth Selenide

The quantum spin Hall phase was first linked to the spin-orbit interaction and a $Z_2$ topological invariant by Kane and Mele\textsuperscript{2}, specifically using graphene as a system\textsuperscript{25} in 2005, who along with Fu then extended their work to three-dimensional materials and predicted the existence of strong topological insulator materials that would be robust against disorder and support spin-polarized conductive surface states\textsuperscript{26}. These predictions were supported by theorists such as Moore and Balents\textsuperscript{27} and Roy\textsuperscript{28}. In 2008, Fu and Kane\textsuperscript{5} then predicted that the conductive surface states of 3D topological insulators proximatized by superconductors would be able to host Majorana bound states. Understandably, all this generated intense interest in the condensed matter community, and the search for real-world 3D topological insulators progressed at a rapid pace. Materials such as bismuth antimonides, bismuth chalcogenides, antimony telluride, and strained mercury telluride\textsuperscript{3,29,30} were predicted candidates for topological insulators, and by 2008, Hsieh et al.\textsuperscript{31} used angle-resolved photoemission spectroscopy (ARPES) to image the band structure of Bi$_{0.9}$Sb$_{0.1}$ and identified the characteristic signature of a topological insulator. In 2009, Xia et al.\textsuperscript{32} also used ARPES to show much the same with Bi$_2$Se$_3$: a Fermi surface for the surface states that is singly degenerate and encloses a single $\bar{\Gamma}$ point in the Brillouin zone. The surface states of topological insulators also exhibit Dirac-like dispersion, which makes them highly conductive. Fig. 3.1 provides a schematic representation of the energy structure of a topological insulator.

Since their discovery in real-world materials, experimental research into topological insulators has flourished. In addition to research into the topological quantum computing and spintronics applications mentioned in Section 1.2.1, Bi$_2$Se$_3$ has a number of other published uses, including as lossless interconnects for electronics\textsuperscript{4}, photodetectors\textsuperscript{33,34}, and as an excellent thermoelectric material, as a result of its bulk bandgap hindering thermal conductivity but its surface states enabling easy electron transport\textsuperscript{35-3839}.\textsuperscript{39}

\textsuperscript{39}It is worth note that Bi$_2$Se$_3$ was known as a thermoelectric material before the discovery of topological insulators, but the framework of topological insulators helps explain how it can simultaneously satisfy being both a thermal insulator and electronic conductor.
Figure 3.1: Conceptual diagram of band structure of a topological insulator, showing bulk bandgap and spin-polarized conductive surface states with Kramers degeneracy.

3.3. Experimental Methods

3.3.1. Sample Preparation

Nanostructures of Bi$_2$Se$_3$ were mechanically exfoliated from bulk Bi$_2$Se$_3$ obtained from Alfa Aesar (99.999% purity) using 1 Mil low-residue blue poly tape$^{40}$. Bi$_2$Se$_3$ samples were directly exfoliated onto SiO$_2$ wafer fragments for AFM analysis. To prepare samples for TEM analysis, the mechanically-exfoliated Bi$_2$Se$_3$ was positioned and transferred to 100 nm-thick using the PMMA and PDMS techniques outlined in Chapter 2. In between all measurements, samples were stored in a vacuum desiccator to reduce the effects of oxidation.

3.3.2. Materials Analysis

For TEM experiments, samples were analyzed using the JEOL 2010F electron microscope operating at 200 kV. Samples were measured in both possible chip orientations, which are shown in Fig. 3.2.

$^{40}$Manufacturer unknown
The face-down configuration shown in Fig. 3.2(a) was used for obtaining high resolution TEM images. On the other hand, the face-up configuration shown in Fig. 3.2(b) maximizes the signal to the EDS detectors and was therefore used when determining elemental ratios.

AFM experiments on Bi₂Se₃ were performed with the NBIC Bruker Dimension Icon in tapping mode.

3.4. Bismuth Selenide Nanosculpting

3.4.1. Introduction

Many of the most interesting proposals for nanoelectronic devices require precise control of the properties of nanostructures, particularly their shape and size. While the simplest applications may require only that a wire or bar of some material have specific dimensions, more advanced devices often demand more advanced geometries. This is indeed the case for nanodevices made from Bi₂Se₃ and other topological insulators that could exploit their more exotic properties. Proposals with far-reaching applications such as fault-tolerant topological quantum computing, near-lossless interconnects in integrated circuits, and thermoelectric devices far more capable than present implementations all require the ability to fabricate structures including wires with...
precisely-controlled dimensions, antidot lattices with specific spacings, and carefully patterned defects. Tuning the thickness across different regions of the device may also permit additional control over transport phenomena. While bottom-up growth of nanostructures in the necessary three-dimensional geometries and defect densities would be ideal, controlled high-yield growth of such complex devices is complicated by the fact that most growth methods yield nanostructures in a great variety of shapes and sizes within the same batch. This presents major challenges to the ability to fabricate devices to exact specifications and imposes limits on the future scalability of geometry-dependent devices. However, top-down processing methods may provide a viable alternative. Standard techniques such as optical and e-beam lithography followed by chemical, plasma or reactive ion etching provide one avenue for forming custom geometries, but dry milling with particle beams presents an interesting and highly-flexible alternative. Resist-based lithographic techniques affect all exposed parts of a homogeneous device in a fairly uniform manner, so many individual layers may be required in order to produce the desired outcome. On the other hand, particle beam dry-milling techniques such as laser milling, focused ion beam (FIB) milling, and TEM nanosculpting are all direct-write methods, which allows for on-the-fly modifications to patterns as well as the ability to create arbitrary shapes and thickness variations in a single step. Additionally, direct-write ion implantation methods may also present the possibility for precise control over doping and defect levels across a device.

Prior to my work, transport studies of FIB-milled nanowires of Bi$_2$Se$_3$ demonstrated that the patterned structures exhibited increased room-temperature photoconductivity and retained signatures of their topological surface states at low temperature. However, some ambiguity about the nature of these wires remained, as transport results implied that the width of the topologically-insulating material was less than the observed width of the wires themselves. So for my first foray into Bi$_2$Se$_3$ nanosculpting, I sought to clarify the effects of gallium-based FIB exposure on Bi$_2$Se$_3$ as well as the reason for the reduced effective size of FIB-sculpted nanowires using high-resolution TEM, EDS, selected-area electron diffraction (SAED), and AFM.

My second project concerned using TEM nanosculpting to pattern Bi$_2$Se$_3$. TEM nanosculpting techniques have previously been utilized with metal thin films and two-dimensional materials. TEM nanosculpting presents a few potential advantages compared to FIB milling for fabrication of advanced devices. First, since TEMs by definition use electrons rather than ions,
accidental and undesirable doping via ion implantation (see and Sharma et al.\textsuperscript{59}, Saji et al.\textsuperscript{64}) is avoided, and beam damage may be ameliorated by a post-fabrication annealing step\textsuperscript{59}. Second, while FIB techniques begin to struggle with resolution at around the 10 nm mark\textsuperscript{52}, TEM sculpting has been shown to be able to provide nanometer-scale control with only highly-localized damage to the structure\textsuperscript{55–58,61–63}. My work, however, was the first to apply this promising technique to Bi\textsubscript{2}Se\textsubscript{3}\textsuperscript{65}.

3.4.2. Experimental Methods

For FIB nanosculpting experiments, we used a FEI Strata DB235 focused ion beam releasing Ga\textsuperscript{+} ions at 30 kV and 10 pA beam current. A conceptual diagram of the layout of the FIB as well as the different directions in which the sample pointed during milling is shown in Fig. 3.3. In Fig. 3.3(a), the sample was milled directly down the [001] axis by pointing the substrate towards the Ga\textsuperscript{+} source within the FIB apparatus. The sample was also milled at an angle by instead pointing towards the in-unit SEM, shown in Fig. 3.3(b). TEM and AFM analysis was performed as outlined in Section 3.3.2.

![Figure 3.3: Diagram of FIB milling setup with (a) Bi\textsubscript{2}Se\textsubscript{3} flake aimed towards the focused ion beam for straight-on milling and (b) Bi\textsubscript{2}Se\textsubscript{3} flake aimed away from the focused ion beam for angled milling.](image)

For performing TEM nanosculpting, we used Gatan Digital Micrograph and DigiScan to control the beam and define write windows. During the sculpting process, the JEOL 2010F was operated in scanning mode, in which the beam was focused to a diameter of 2 nm or less. The scan coils allow
the probe to be positioned on the sample with nanometer precision.

The majority of samples presented employed the “spot drilling” mode, in which a beam current of $0.4 \times 10^9 \text{ A m}^{-2}$ was used. The beam was placed in spot mode, and the stationary beam was then positioned on the desired area of the sample. The beam was held at this location for 3 min to 6 min before another scanned image was collected so that progress could be monitored and the position of the probe updated if necessary. Depending on sample thickness, beam current (some samples were spot drilled at $4.8 \times 10^9 \text{ A m}^{-2}$), and focus, it took between 3 min and 15 min to drill through a Bi$_2$Se$_3$ flake completely.

For the samples that were thinned in the TEM rather than drilled, I used the following procedure, adapted from Rodríguez-Manzo et al.\textsuperscript{66}. First, the free lens settings of the microscope were modified to produce a beam current of $4.8 \times 10^9 \text{ A m}^{-2}$. This change negatively affects resolution, but it is strongly recommended in order to minimize process time. Then, I centered the write window on a chosen area, set the size of the window and the magnification of the microscope (typically 84 nm $\times$ 84 nm) to define the thinning region, and increased the pixel time to 10 $\mu$s. The region was then scanned continuously in imaging mode for intervals of 15 min until the observed change in the STEM image was considered sufficient for analysis. The process time for this technique varied considerably depending on the area of the thinned region and the desired depth of thinning. For a smaller area and a thinning depth of 1 nm to 30 nm, the process could take as little as half an hour, whereas thinning a larger area (e.g., 0.2 $\mu$m $\times$ 0.1 $\mu$m) to a depth of $>100$ nm took several hours.

In order to take profiles accurately along the lattice vectors in Digital Micrograph, the DiffTools script was first downloaded and installed. Then, the “Measure Spacings and Angles” tool was used on the FFT of the HR-TEM image under study. Not only does this useful tool provide the direct-space distance corresponding to the measurement from the central spot to the $n^{th}$ order spots in question (or between two $n^{th}$ order spots—you can arbitrarily pick the measurement points and the angle between them), but it also draws helpful yellow lines between the spots. These lines point in the direction of the reciprocal lattice vectors, so one can simply copy them from the markup FFT onto the direct-space HR-TEM image, read off its measurements to get the slope, draw a profile line with the same slope, and\textsuperscript{41} you have a profile measurement that is accurately orthogonal to a set of lattice planes.

\textsuperscript{41}Bob’s your uncle
To accomplish this in Digital Micrograph, import the DiffTools script and use its “Measure spacings and angles” feature on the FFT of the image.

3.4.3. FIB Milling Results

In order to characterize the milling behavior of the FIB, a dose test was performed. An AFM scan and the depth per dose of this test can be seen in Fig. 3.4. Each individual square shown in Fig. 3.4(a) was milled for a different time, between 4 s and 28 s. The milled regions had a roughness of less than 1 nm, which compares favorably to the roughness of argon plasma etching, which exceeds 2 nm for any etch time beyond a few seconds. The mill rate in Fig. 3.4(b) remains roughly constant until a depth of 110 nm. After that mark, the FIB appears to have milled through the Bi$_2$Se$_3$ and began attacking the underlying substrate. Under 110 nm, the linearity of the depth vs mill dose suggests that sample heating during exposure was minimal.

![Figure 3.4: Bi$_2$Se$_3$ straight-on dose test using Ga$^+$ focused ion beam at 10 pA setting. (a) AFM image of the Bi$_2$Se$_3$ flake on SiO$_2$ substrate. Each square is approximately 4 µm$^2$ in area. (b) Plot of depth as a function of FIB beam dose. The dashed blue line represents the approximate dose at which the beam milled entirely through the Bi$_2$Se$_3$ and began milling the SiO$_2$.](image)

A thinned sample on a SiN$_x$ substrate was also prepared in order to probe the crystal structure of milled Bi$_2$Se$_3$. AFM and a graph of depth vs ion dose is shown in Fig. 3.5. Once again we can see a linear depth vs dose regime that corresponds to ablation of the Bi$_2$Se$_3$ flake, followed by a dropoff once the ion beam begins to encounter the SiN$_x$ window. It can readily be calculated from the time doses and the probe current of 10 pA that the doses for the different regions of the flake range from $1 \times 10^{15}$ cm$^{-2}$ to $2 \times 10^{16}$ cm$^{-2}$.

Fig. 3.6 shows the results of EDS and SAED analysis for the thinned flake. The numbered regions
Figure 3.5: Mill depth vs dose from AFM map of Bi$_2$Se$_3$ sample prepared on SiN$_x$ for TEM analysis. (a) AFM image of the FIB-thinned sample. (b) Mill depth vs dose. Dashed blue line indicates the approximate dose at which the beam had removed the Bi$_2$Se$_3$ entirely and began milling the SiN$_x$.

in Fig. 3.6(a) correspond to the doses shown in Fig. 3.5(b) (green-colored regions all correspond to the dose point 0 s/cm$^2$, as they were unmilled). The ion milling had an obvious effect on both the brightness of the different regions of the flake and on the number of x-ray counts measured by the EDS detector during its line scan. While the first milled region, subject to a dose of $1 \times 10^{15}$ cm$^{-2}$ shows a minimal change in the count ratio of selenium to bismuth, regions subjected to higher doses exhibit a decline in the Se:Bi ratio, which indicates preferential removal of selenium. Given that selenium is a considerably lighter element than bismuth (the heaviest effectively stable element), this result is unsurprising. The smallest ratio is found at the small amount of leftover material 5.5 µm from the start of the line scan. At this distance, the signature from the bismuth atoms dominates, which is the reverse of what would be expected from Bi$_2$Se$_3$’s stoichiometry. Gallium signals were observed only in the areas below region 8, which had been milled to a thickness of under 10 nm. This result suggests that the Ga$^+$ ions largely pass through the Bi$_2$Se$_3$ flake and instead embed in the silicon nitride window.

Fig. 3.6(c), (e), (g), and (i) all show diffraction patterns from unmilled regions of the flake, all of which exhibit the characteristic six-fold rotational symmetry and have diffraction spacings relatively consistent with the published value of 0.21 nm for the $\{1120\}$ planes of Bi$_2$Se$_3$ and when analyzed, all four yield a lattice parameter of $a = 0.432$ nm, which is somewhat larger than the published value of $a = 0.414$ nm.

The SAED images from regions 2 and 4, Fig. 3.6(d) and (f), respectively, show both the hexagonal
pattern and a distinct ring with a diameter of 6.3 nm\(^{-1}\). Fig. 3.6(d) has a lattice constant of \(a = 0.431\) nm, and Fig. 3.6(f) has a lattice constant of \(a = 0.439\) nm, slightly larger than in the unmilled areas. The SAED image from region 6, Fig. 3.6(h), shows the hexagonal pattern of \{11\(\bar{2}\)0\} planes of Bi\(_2\)Se\(_3\), which yield a lattice constant of \(a = 0.437\) nm. This set of spots also has a ring associated with it, which may imply the Bi\(_2\)Se\(_3\) has been pulverized. In addition, there is a bright inner ring with a radius of 0.320 nm. If this is analyzed as a ring of \{11\(\bar{2}\)0\} planes of Bi\(_2\)Se\(_3\), a lattice constant of \(a = 0.370\) nm is obtained, which strongly suggests that the inner ring is instead from a different material.

The diffraction pattern from region 8 (Fig. 3.6(j)) shows both the 6.3 nm\(^{-1}\) ring and some evidence of polycrystalline Bi\(_2\)Se\(_3\). The polycrystalline structure is indicated by a ring of diffraction spots with a diameter of 9.1 nm\(^{-1}\), which corresponds to a spacing of 0.22 nm. The smoother 6.3 nm\(^{-1}\) diameter ring in the milled regions suggests that the ablation creates an amorphous or fine-grained surface, and given the preferential removal of selenium, this surface is likely primarily composed of bismuth. 6.3 nm\(^{-1}\) equates to a spacing of 0.32 nm in direct space. This spacing as well as the similar ring from Fig. 3.6(h) may correspond either to a bismuth oxide layer formed from air exposure after the sample was removed from the FIB\(^{69,70}\) or to recrystallized elemental bismuth\(^{71,72}\).

EDS and SAED results for using FIB milling to sculpt wires of various thickness from a Bi\(_2\)Se\(_3\) flake are presented in Fig. 3.7. Fig. 3.7(a) shows the counts per second EDS image of the sample, which had eight wires of widths ranging from 260 nm to 26 nm. Areas in which the ion beam cut through the Bi\(_2\)Se\(_3\) entirely and began to mill the Si\(_3\)N\(_4\) window appear as lighter gray rectangles between the wires. The lighter color indicates the presence of gallium atoms embedded in the substrate. A gallium signal also appears quite dramatically in Fig. 3.8.

Returning to Fig. 3.7, the wires in (a) that are labeled from 1 to 4 were selected for further analysis, and their SAED patterns appear in Fig. 3.7(c-f), with their selected areas inset. It is apparent that as the wires decrease in width, the Bi\(_2\)Se\(_3\) diffraction spots disappear. For wire 3 (width 120 nm), only one pair of blurred spots that might correspond to distorted Bi\(_2\)Se\(_3\) planes can be seen, and no Bi\(_2\)Se\(_3\) can be discerned at all in the pattern for wire 4 (width 26 nm). The disappearance of the Bi\(_2\)Se\(_3\) \{11\(\bar{2}\)0\} spots and the emergence of spots with spacings similar to those observed in the thinned regions in Fig. 3.6 suggests that as the wire width decreases, defected or recrystallized material composes an increasing proportion of the wire. These edge regions could be the result of
Figure 3.6: TEM image, EDS trace, and SAED spots from eight regions of the thinned flake. Green circles indicate the \{10\bar{1}0\} planes of Bi$_2$Se$_3$, and wine circles indicate the \{11\bar{2}0\} planes. (a) Counts per second image of thinned Bi$_2$Se$_3$ flake. Unmilled regions of the flake appear highlighted in green. (b) Trace of EDS intensities of bismuth (blue) and selenium (red) across the sample. The path of the trace is represented by the red arrow pointing across the flake in (a). (c) Diffraction from bulk crystal in region 1. (d) Diffraction from region milled for 1 s, region 2 in (a). (e) Diffraction from region 3 of (a). (f) Diffraction from a strip milled for 5 s, listed as region 4 in (a). (g) Diffraction from region 5 of (a). (h) Diffraction from region 6 of (a). (i) Diffraction from region 7 of (a). (j) Diffraction from region 8 in (a), which was thinned for 10 s.
Figure 3.7: Bi$_2$Se$_3$ flake cut into wires and analyzed using EDS and SAED. Green circles indicate the \{10–10\} planes of Bi$_2$Se$_3$, and wine circles indicate the \{1120\} planes. Light blue and violet circles indicate spots of unknown provenance. (a) Counts per second image of Bi$_2$Se$_3$ wire sample. (b) SAED pattern with selected area inset of unmodified Bi$_2$Se$_3$ flake. (c) SAED of wire 1, width 260 nm, with inset of selected region. (d) SAED of wire 2, width 160 nm, with selected area inset. (e) SAED of wire 3, width 120 nm, with selected area inset. (f) SAED of wire 4, width 26 nm, with selected area inset. (g) EDS phase map of wire sample. Blue represents regions containing Bi and Se, and red represents their absence.

The destruction of the Bi$_2$Se$_3$ crystal as a function of wire width is further evinced by the EDS phase mapping shown in Fig. 3.6(g). In this phase map, blue areas represent regions containing Bi, Se, and Si, where as the red areas represent the presence of Si only. While the gallium signal is observable in the elemental maps, it is not strong enough that the EDAX TEAM software distinguished it in the phase map. As can be seen, wire 4 is not recognized as different from the substrate. This indicates that although some material remains in the area, as can be seen in the counts per second image, the wire might not be composed of Bi$_2$Se$_3$. Similarly, the diffraction pattern in Fig. 3.6(f) shows no evidence of Bi$_2$Se$_3$ crystal structure. Our results are comparable to the transport results presented in Bhattacharyya et al.\textsuperscript{54}. In their article, the authors observe Aharonov-Bohm oscillations in FIB-cut nanowires that have a period associated with wire cross-sections smaller than their physical cross-sections, indicating damage to the wires from the FIB milling. While the authors of the study suggested that this result was due to deformations and cracking or Ga$^+$ ion implantation; our
Figure 3.8: EDS images of Bi$_2$Se$_3$ flake milled into an array of nanowires. (a) Counts per second image of the flake. The box indicates the mapped region. (b) Bismuth elemental map. (c) Selenium elemental map. (d) Gallium elemental map.

results suggest that the dominant factor is simple defect creation and material destruction, which is supported by the minimal gallium signal in the EDS of the thinned sample and by the disappearance of the Bi$_2$Se$_3$ diffraction spots as a function of wire width. We also observed no evidence of large scale cracking as a result of the ion milling, which would appear as splitting in the SAED patterns and as visible cracks in the TEM images of the wires.

In order to look more carefully at the material along the wire edges and the structure of wire 4, we collected HR-TEM images. These images and their FFTs are presented in Fig. 3.9. The HR-TEM image of the edge of wire 2 is shown in Fig. 3.9(a) with its FFT inset. The wire “edge” is defined as the approximately 20 nm-wide region inwards from the visible physical boundary of the wire, which is denoted in Fig. 3.9(a) by dashed lines. The difference between the edge region and the bulk of the wire can be seen in Fig. 3.9(b-c), which show FFTs from the interior (wine) and edge (light blue) regions respectively. The FFT in Fig. 3.9(b) shows a hexagonal pattern with lattice constant of a
Figure 3.9: High-resolution TEM and FFT images of wires. Wine circles indicate the \{11\overline{2}0\} planes of Bi$_2$Se$_3$, and violet circles indicate unknown spots. (a) HRTEM of edge of wire 2 from Fig. 3.7(a). The edge of the wire is marked as between the dashed red lines. Inset is the FFT for the entire image. (b) FFT of region 1 (wine box) in (a). (c) FFT of region 2 (light blue box) in (a). (d) HR-TEM image of the edge of wire 4 from Fig. 3.7(a). (e) FFT of (d).

= 0.401 nm, which is somewhat similar to that observed in bulk Bi$_2$Se$_3$ (0.414 nm$^{68}$). However, the FFT of the edge region shown in Fig. 3.9(c) instead shows a single pair of spots with a spacing of 0.302 nm. This clearly indicates that this region has something other than \{11\overline{2}0\} planes of Bi$_2$Se$_3$ viewed down [001]. A similar treatment of wire 4, whose width is on the order of the edge region observed in the larger wires, is shown in Fig. 3.9(d-e). While a single pair of Bi$_2$Se$_3$ \{11\overline{2}0\} lattice spots is observed, they are not the dominant signal. Close inspection of the HR-TEM image reveals islands of Bi$_2$Se$_3$ within wire 4, but they are isolated from each other and compose only a small fraction of the material. Instead lattice planes of spacing 0.307 nm similar to those observed at the edges of the other wires and milled regions dominate.

This finding further supports the results from Fig. 3.7(f-g): the HR-TEM and FFT of the wire edges clearly indicates that while some crystal order exists, the edges are predominantly something other than Bi$_2$Se$_3$. This material might also be a bismuth oxide$^{69,70}$ or crystalline bismuth$^{71,72}$. However, the material adjacent to the edge might not directly characterize the edge itself.

To study the effect the ion beam has on the edges it creates during milling without the interference
of excess material, another flake of Bi$_2$Se$_3$ was prepared by milling it at an angle. Cutting the material at an angle away from the flake will sputter material away from the flake and leave a surface that is minimally affected by the beam, as outlined conceptually in Fig. 3.10. TEM and AFM results from the angle-cut sample are shown in Fig. 3.11. The white circle on the AFM image in Fig. 3.11(a) indicates the primary analyzed region, as the sample was milled in multiple locations. In this region, the beam was incident from the right at an angle of 52° from the substrate normal. Fig. 3.11(b) shows diffraction from this region, with the direct-space selected area shown in the inset. The diffraction pattern maintains the six-fold symmetry and has a lattice constant of $a = 0.428$ nm. Unlike the thinned regions presented in Fig. 3.6, no amorphous or polycrystalline rings appear, which indicates that the angle-cut surface is minimally disturbed. In an AFM slice taken from this region, shown in Fig. 3.11(c), we find that the beam (direction shown by green arrow) also milled into the Si$_{N_x}$ window. The surface of the cut is smooth, and the angle of the cut relative to the substrate normal is 58°.

HR-TEM imaging of the thinnest regions of the cut, which have the highest proportion of damaged
Figure 3.11: TEM and FFT images and analysis of a Bi$_2$Se$_3$ flake cut at a 52° angle from substrate normal. For the diffraction and FFT patterns, Wine circles indicate the Bi$_2$Se$_3$ (1120) spots, and light blue and violet spots indicate spots of unknown origin. (a) AFM image of cut flake. (b) SAED image of region circled in (a). Inset is the image of the actual selected area used. (c) Height vs. position profile from the red circled region in (a). The green arrow indicates the approximate beam direction relative to the sample during cutting. (d) HR-TEM image of an edge within the circled region in (a). The violet-dashed line indicates the location of the edge, apparent in both the image and its FFT. (e) FFT of region 1 (wine box) in (d). (f) FFT of region 2 (light blue box) in (d). (g) FFT of region 3 (gold box) in (d). (h) FFT of region 4 (green box) in (d). (i) FFT of total image in (d).

Material compared to crystalline Bi$_2$Se$_3$, is shown in Fig. 3.11(d). The FFT of this entire region (Fig. 3.11(i)) shows lattice spots corresponding to multiple crystal phases, including but not limited to Bi$_2$Se$_3$. The lattice parameter from the Bi$_2$Se$_3$ spots is $a = 0.420$ nm. The spacings for the unknown spots are 0.156 nm and 0.308 nm. This result is dissimilar to the SAED pattern, which shows only Bi$_2$Se$_3$. The FFTs from specific regions of the sample, indicated by the colored boxes in Fig. 3.11(d), illustrate the changeover from the thicker Bi$_2$Se$_3$-dominant regions to the end of the cut, which is much thinner and where the crystal structure varies considerably (at approximately the 0.8 µm mark in Fig. 3.11(c)). The end of the Bi$_2$Se$_3$ flake is denoted by the violet dashed line in Fig. 3.11(d), which is the point at which no lattice spots or other indications of order were observed in either the direct-space image or FFT. FFT of the thicker regions, Fig. 3.11(e, f), clearly show Bi$_2$Se$_3$ spots with six-fold symmetry and lattice parameters of $a = 0.410$ nm and 0.407 nm, close to the literature value of Bi$_2$Se$_3$ but significantly smaller than the value measured in the SAED.
pattern. Given this discrepancy, and the similarity of the value from Fig. 3.11(b) to the values found in Fig. 3.7 for well-defined Bi$_2$Se$_3$ regions, there may have been a systematic error in the calibration of the TEM’s camera length.

The edge regions, on the other hand, show different patterns. Fig. 3.11(g) shows two pairs of nearly-superimposed lattice spots with a spacing of 0.221 nm, similar to (but still significantly larger than) the spacing for the \{1120\} planes of Bi$_2$Se$_3$, while Fig. 3.11(h) shows the previously-observed spacing of 0.310 nm, as well as another set of spots at 0.155 nm, which, at exactly half the length, are almost certainly the first-order spots. This result shows that in the thinner regions near the physical edge of the flake, crystalline Bi$_2$Se$_3$ coexists with one or more different crystalline phases that are not observed in thicker regions. The results from the four regions analyzed show that even though the flake has been ablated by the FIB beam, the face of the cut has not been greatly affected. Thus the “edge” regions from the wires are most likely left-over material from the face-on milling, and the sidewalls were not strongly affected in an observable way using our methods.

### 3.4.4. TEM Nanosculpting Results

![Figure 3.12: STEM images of a Bi$_2$Se$_3$ flake as it is cut to create a small T-junction. (a-d) Images taken sequentially during STEM drilling. The Bi$_2$Se$_3$ flake appears light gray on a black SiN$_x$ background. (e) Phase-contrast TEM image of final structure. (f) SAED of initial structure at drilling site with selected area inset, aligned to [001] zone axis with lattice constant $a = 0.409$ nm. The red-circled spot was used for dark-field imaging. (g) Dark-field image of initial Bi$_2$Se$_3$ (colorized) (h) SAED of final T-junction with selected area inset. Lattice constant is $a = 0.411$ nm. The red-circled spot is again used for dark-field imaging. (i) Dark-field image of final nanostructure (colorized). Red arrow indicates location of T-junction.](image-url)
Fig. 3.12 documents the process of TEM nanosculpting a Bi$_2$Se$_3$ flake using the “spot drilling” method in the face-down orientation within the TEM. For this technique, the scanning probe parks on a single, user-defined region of the sample for localized ablation and is then repositioned to the user’s fancy. The dark-field STEM images of Fig. 3.12(a-d) show the flake at various stages of the drilling process. The end result, shown in Fig. 3.12(e), is a T-junction of approximate length 80 nm, width 20 nm, and junction thickness 30 nm. Fig. 3.12(f, g) show selected area diffraction and dark-field images of the flake before electron beam modification. The lattice spacing is 0.205 nm, and the lattice parameter is $a = 0.409$ nm. The colorized dark-field image in Fig. 3.12(g) was taken using the circled diffraction spot. Similarly, Fig. 3.12(h, i) present the selected area diffraction and colorized dark-field image of the flake after sculpting the T-junction. In Fig. 3.12(h) the measured lattice spacing of the $\{1\bar{1}20\}$ planes is 0.201 nm, which corresponds to a lattice parameter of $a = 0.411$ nm. These values agree well with the known lattice spacing of 0.21 nm for the $\{1\bar{1}20\}$ planes of Bi$_2$Se$_3$ and the published value of the lattice parameter $a = 0.414$ nm. Splitting appeared in the lower three spots of the pattern in Fig. 3.12(h), which may indicate that the lattice planes shifted across a dislocation. However, the darker band stretching from the T-junction into the body of the flake shown in Fig. 3.12(i) indicates continuity along the selected lattice vector.

A second T-junction was sculpted at $4.8 \times 10^9$ A m$^{-2}$, and the process images and results can be seen in Fig. 3.13. The six-fold rotational symmetry of Bi$_2$Se$_3$ mostly remains after sculpting, but the lattice spacing is $a = 0.438$ nm, which is a considerable increase over the published value and the measurement from the first T-junction in Fig. 3.12. The lengthy exposure time for this thicker flake has compromised the structure somewhat, apparently.
Figure 3.13: STEM images of second Bi$_2$Se$_3$ nanoflake as it is sculpted to create a small T-junction. In this trial, the probe current was set to $4.8 \times 10^9$ A m$^{-2}$ for cutting. (a) Image of the flake prior to sculpting. (b) Image of the flake after 6 min beam exposure. (c) Image of the flake after 12 min beam exposure. (d) Image of the flake after 18 min beam exposure. (e) Image of the flake after 24 min beam exposure. (f) Image of the flake after 30 min total beam exposure. (g) TEM image of the final structure. (h-k) SAED of T-junction.

In addition to the T-junctions, I sculpted structures including a long wire, a short wire, an annulus, a constriction, and a small antidot array using the same “spot drilling” process. Figs. 3.14 and 3.15 provide HR-TEM images of these structures, with Fig. 3.15 showing the regions subject to beam ablation highlighted in green. Additionally, FFTs of these images are shown in Fig. 3.16. These data suggest the preservation of the intralayer hexagonal crystal structure even after considerable sculpting. In general, the 6-fold rotation symmetry survives, and the measured lattice spacings remain consistent with the {1120} planes of bismuth selenide. For the large wire (Fig. 3.16(a)), the lattice parameter measured was $a = 0.415$ nm, and the smaller wire of Fig. 3.16(b) indicated a lattice parameter of $a = 0.407$ nm. The FFT of the ring shown in Fig. 3.16(c) had a lattice constant of $a = 0.410$ nm; that of the constriction shown in Fig. 3.16(d) had a lattice constant of $a = 0.406$ nm; and that of the antidot lattice had $a = 0.403$ nm.
Figure 3.14: HR-TEM of nanosculpted structures on a SiN_x substrate. (a) A 15 nm wire. (b) A thinner, shorter wire, boxed in red. (c) A ring. (d) An antidot array.

Figure 3.15: Fig. 3.14 with areas subject to the beam for nanosculpting highlighted in green.
In Fig. 3.16(c) and 3.16(e) the intensities of the Bi$_2$Se$_3$ spots varies, and in Fig. 3.16(d) a new pair of spots, corresponding to a spacing of 0.360 nm. While this could correspond to a bismuth oxide or elemental bismuth,$^{60}$ the spot is at the correct distance from the center and at the correct angle to be a \{10\bar{1}0\} spot of Bi$_2$Se$_3$. The absence of the phases that formed during FIB milling attests to the improved cleanliness of this technique.

Figure 3.16: FFTs of the images shown in Fig. 3.14. Scale bars on the inset images are all 20 nm. Green circles indicate \{1010\} spots of Bi$_2$Se$_3$, and wine circles indicate Bi$_2$Se$_3$'s \{1120\} spots. (a) FFT of the larger nanowire. (b) FFT of the smaller nanowire, taken from the wine-boxed region of interest in the direct space image. Spots are faint due to the small size of the ROI. (c) FFT of the ring nanostructure. One pair of spots shows twinning. (d) FFT of the constriction/point contact. One pair of Bi$_2$Se$_3$ spots has disappeared, and a new pair of spots with a spacing of 0.360 nm from the center appeared. This new pair of spots corresponds with a set of Bi$_2$Se$_3$ \{1010\} planes. (e) FFT of the antidot lattice. All six second-order spots are visible, but one pair is very faint.

In general, the edges of the TEM nanosculpted regions appear free of redeposited or recrystallized material, and the lattice planes for Bi$_2$Se$_3$ can be observed not only within the bulk of the material, but also at the edges. The analysis shown in Fig. 3.17 supports the presence of crystalline Bi$_2$Se$_3$ within nanometers of the drilled regions with considerably less deviation from the published value than observed in Fig. 3.13. Fig. 3.17(b) indicates a lattice parameter of $a = 0.440$ nm, and Fig. 3.17(d-e) indicate lattice parameters of $a = 0.407$ nm and 0.406 nm, respectively.
Figure 3.17: Direct-space images and FFTs of beam-exposed edges of TEM nanosculpted Bi$_2$Se$_3$. (a-b) Wine-boxed ROI and FFT of the inner edge of the sculpted annulus. The FFT is very faint because the ROI is small and because within the ROI, the proportion of Bi$_2$Se$_3$ as opposed to amorphous SiN$_x$ is small. (c) HR-TEM image of the antidot lattice with two regions of interest (wine and light blue boxes). (d) FFT of the wine-boxed region, showing the clear presence of Bi$_2$Se$_3$ $\{11\bar{2}\}$ lattice spots (wine circles). (e) FFT of the light blue-boxed region, showing much the same as (d), but the Bi$_2$Se$_3$ $\{11\bar{2}0\}$ spots are in light blue. As in (b), the FFT spots in (d) and (e) are faint due to the small sizes of the regions of interest and because the majority of the regions are taken up by the central hole, rather than the edges.

Selected-area diffraction patterns also support the continued existence of crystalline bismuth selenide in the drilled regions, as can be seen in Fig. 3.18. The lattice constant for the total region is $a = 0.400$ nm, whereas the lattice constants for each individual area are slightly but significantly higher, at $a = 0.404$ nm for the constriction, $a = 0.409$ nm for the long wire, and $a = 0.403$ nm for the antidot lattice, which suggests that beam damage may lead to a looser lattice, although the difference is small.

A second TEM sculpting technique was also employed in which the probe current was increased to $4.8 \times 10^9$ A m$^{-2}$ and then rastered across a defined area repeatedly rather than manually moved from point to point. The idea for this technique was to enable smoother-cut lines than were possible using
spot mode. An overview of the results of this technique can be seen in Fig. 3.19. Fig. 3.19(a) shows an AFM topography scan of the flake subject to TEM thinning (green and yellow boxes) as well as a spot-drilled line across the flake (blue oval). The decrease in height in the thinned regions is about 20 nm and comes with an increase of surface roughness \( (R_q) \) from 1.4 nm to 3.5 nm in and around the thinned regions. The depth profile in the yellow-boxed region is limited by the horizontal resolution of the TEM. This result compares very favorably with argon plasma etching, which can introduce height fluctuations as great as 20 nm\(^{48}\). On the other hand, the area around the line subject to spot drilling shows no increase in surface roughness or surface damage in the surrounding areas, which is consistent with our assertion that TEM spot drilling causes only highly localized damage. The AFM of the green-boxed region in Fig. 3.19(c) also suggests that less severe thinning may be used to introduce surface disorder, which may have implications for controlling transport via charge trapping and slowing surface conduction\(^{46}\). Fig. 3.19(b) shows a low-magnification TEM image of the same flake (mirrored, due to its “upside down” orientation in the TEM), with the same regions

Figure 3.18: Direct space and SAED images of TEM-drilled nanostructures. For the selected-area diffraction images, the wine circles indicate the Bi\(_2\)Se\(_3\) \{1120\} diffraction spots. All inset scale bars are 50 nm. (a) Low-magnification phase-contrast TEM image of the patterned flake. Red arrows point towards the wire+annulus, the constriction, and the antidot lattice. (b) SAED image of the wire, annulus, and inner edge of the Bi\(_2\)Se\(_3\) flake. (c) SAED image of a sculpted constriction, with selected area inset. (d) SAED image of the lower portion of the long sculpted wire and a second constriction, with selected area inset. Lattice constant is (e) SEAD image of the antidot lattice with selected area inset.
Fig. 3.19(c) shows a close-up of the spot-drilled line from the upper-left-hand corner of the flake. There is some roughness evident in the trench, but there is no obvious effect on the broader structure. Finally, Fig. 3.19(d) and (e) show a close up of the thinned regions and the FFT of the red-boxed region of interest, respectively. All six \{11\overline{2}0\} Bi$_2$Se$_3$ lattice spots are visible, and analysis yields a lattice constant of $a = 0.405\,\text{nm}$.

Figure 3.19: Results of thinning Bi$_2$Se$_3$ by rastering over an area. (a) AFM of thinned flake. Due to its orientation (face-up in the AFM and face-down in the TEM), the AFM image is mirrored relative to the TEM image. Green and gold boxes indicate regions subject to thinning via an area raster scan. The light blue oval indicates an additional spot-drilled line. (b) TEM image of the flake after sculpting, with pre-sculpting image inset. (c) Higher-magnification image of the spot-drilled line, showing the extended and continuous path. (d) Higher-magnification image of the thinned regions of the flake. The red box indicates the area selected for HR-TEM analysis. (e) FFT of HR-TEM image of red-boxed region in (d), adjacent to where the thinning completely ablated the Bi$_2$Se$_3$. The direct-space image for the FFT is inset, with a scale bar of 20 nm.

Fig. 3.20(a) shows an HR-TEM image of the most severely thinned region of the flake. The region boxed in red is the thinnest areas, and its FFT (Fig. 3.20(b)) still exhibits the six-fold rotational symmetry of Bi$_2$Se$_3$ viewed down the [001] zone axis. The teal, green, and gold boxes indicate 50 pixel-wide regions oriented along the \{11\overline{2}0\} lattice vectors drawn using the method outlined at the end of Section 3.4.2, with like colors corresponding to the circled FFT spots in Fig. 3.20(a) and
the profiles shown in Fig. 3.20(c). The black boxes in each image demarcate the distance across ten lattice fringes. Averaging these measurements yields a lattice constant of \( a = 0.464 \text{ nm} \). These results indicate that even though the surface roughness increases in the thinned regions, and even though these areas have experienced heavy 200 keV electron beam exposure, the material itself still retains its crystal symmetry, although its lattice parameter calculated from the FFT is rather larger: \( a = 0.502 \text{ nm} \).

Selected-area diffraction analysis of the thinned regions also support this conclusion. The SAED results are easier to read and interpret than in the case of the spot-drilled nanostructures because the thinning took place over wide areas that can completely fill the selected area apertures. Not only does this make the signals brighter, it also means that contributions from areas not subject to intense irradiation are largely excluded. The results of imaging thinned regions can be seen in Fig. 3.21. In Fig. 3.21(a), the measured lattice parameter is \( a = 0.428 \text{ nm} \), and the lattice parameter calculated from Fig. 3.21(b) is \( a = 0.425 \text{ nm} \). These results support the above measurements from the FFT of the thinned region, in that extended, large-area beam exposure appears to expand the lattice.

It is important for the sample to face downwards relative to the beam direction during sculpting. If the sample instead faces towards the beam source, material does not sputter away from the Bi\(_2\)Se\(_3\) nanostructure. Instead, it travels or redeposits on the substrate and the flake and forms crystalline structures that are incredibly robust against further TEM irradiation. A conceptual diagram of the difference is presented in Fig. 3.22. These structures can form during both spot-drilling and large-area thinning and form somewhat randomly. SAED of a face-up thinned region is shown in Fig. 3.21(c). The average spacing for the violet-circled spots is 0.166 nm, and the spacing for the light blue-circled spots is 0.283 nm. As this still appears to be a hexagonal crystal viewed down the \([001]\) zone axis, the lattice parameter is \( a = 0.330 \text{ nm} \), which is about 73% of the lattice parameter for Bi\(_2\)Se\(_3\). Given this large difference and that all other experiments with irradiating Bi\(_2\)Se\(_3\) we performed indicated that beam damage caused the lattice to expand, this material is probably distinct from Bi\(_2\)Se\(_3\). Recrystallization and TEM-induced stresses are not unheard of—they have been observed during TEM sculpting of gold and platinum electrodes,\(^{61}\) though we could not observe elongation of the structures along the beam due to the presence of the substrate.

Fig. 3.23 provides a more detailed look into the formation of unexpected structures ("weird persis-
Figure 3.20: Additional analysis of highly-thinned region. (a) HR-TEM image of the most highly-thinned region of the sample. (b) FFT of red-boxed region in (a). The FFT shows preservation of the six-fold rotational symmetry even after truly extensive exposure to the high-current probe beam. (c) Profile plots of part (a), taken in the teal-, green-, and gold-boxed regions. The black boxes on the profile plots enclose 10 lattice fringes.
Figure 3.21: SAED of different Bi$_2$Se$_3$ regions subject to raster-scan TEM thinning. Wine circles indicate the $\{11\bar{2}0\}$ lattice spots of Bi$_2$Se$_3$, and teal and dark pink circles indicate first and second-order spots of an unknown material. All direct-space scale bars indicate a length of 100 nm. (a) SAED of the gold-boxed region in Fig. 3.19, with selected area inset. (b) SAED of the green-boxed region in Fig. 3.19, with selected area inset. (c) SAED of face-up thinned region in Fig. 3.23.

tent stuff") during face-up thinning with a probe current of $4.8 \times 10^9$ A m$^{-2}$. While the exact nature of the material that was formed in Fig. 3.23(b, c) was not determinable in this study, the average lattice plane spacings along each axis of 0.30 nm, 0.32 nm and 0.27 nm might correspond to recrystallized bismuth$^{71,72}$ or to a bismuth oxide$^{69,70}$. Given that these structures formed under vacuum,
Figure 3.22: Conceptual diagram of the results of TEM drilling in both the face-down (left) and face-up (right) configurations. When the sample faces away from the beam source, ejected material is able to sputter away from the sample and escape into the column. When the sample faces towards the beam, sputtered material is not carried away and instead redeposits on or near the sample.

Recrystallized bismuth seems the more likely candidate. Fig. 3.23(c, d) shows a Moiré superlattice that also formed during face-up thinning. It appears to be formed from a hexagonally-symmetric crystal viewed down the [001] zone axis, and if the approximate center of mass of each cluster is treated as the location of the spot, it has a lattice constant of 0.534 nm.

The formation process for weird persistent stuff during face-up spot drilling is shown in Fig. 3.24. At first, the material was carved relatively easily, but as the process continued, the redeposited began to form in large quantities to the point that it eventually made all attempts to sculpt a nanowire impossible.

Fig. 3.25 showcases the truly remarkable resilience of these structures. In Fig. 3.25(a), there is about 60% of a lighter ring surrounding the dot that formed. In this region, the silicon nitride window is completely absent. Unlike the dot, all 100 nm thickness of the window was ablated while the beam was parked directly on the dot for over half an hour in an attempt to determine if carving away the redeposited material was possible. In the end, the window gave way before the dot did, and the dot fell into the TEM column. More examples and FFT analysis of these dots and their strange behavior
Figure 3.23: HR-TEM analysis of an example of “weird persistent stuff” that formed during face-up thinning with a probe current of $3.8 \times 10^9$ A m$^{-2}$. (a) Lower-magnification image of the face-up thinned area. The teal box surrounds the area shown in (b), and the violet box encloses the area shown in (d). (b) A dot of recrystallized material formed during face-up thinning. Its resilience is apparent from its position over a hole drilled entirely through the surrounding Bi$_2$Se$_3$. (c) FFT of the green-boxed region in (b). (d) Image of Moiré fringes formed under face-up irradiation. (e) FFT of (d), showing a superlattice.

under electron beam irradiation can be seen in Fig. 3.26. In the FFT analysis Fig. 3.26(b), the [001] hexagonal pattern shows a lattice constant of $a = 0.518$ nm, and the interior spots have lattice plane spacings of 0.358 nm, 0.778 nm and 0.401 nm, from left to right. In Fig. 3.26(c), unusual behavior in response to beam irradiation can be seen—the dot selected for FFT analysis (violet box) changed its lattice structure dramatically and in a way that looks remarkably like a brick wall. Its FFT, shown in Fig. 3.26(d), appears to be a combination of the expanded hexagonal lattice and a body-centered cubic diffraction pattern viewed down [012], but the small size of the FFT and resulting very closely-spaced and faint spots compared to the noise background made accurate determination of the spacings, angles, and ratios that would be necessary to verify this and extract lattice constants unfeasable.
3.4.5. Conclusions

FIB milling of Bi$_2$Se$_3$ is a promising method for sculpting the topological insulator into application-specific geometries. While FIB thinning the sample creates a uniform and smooth surface, it also causes localized damage that results in partially amorphous selenium-deficient surfaces. The edges created when cutting wires from bulk Bi$_2$Se$_3$ are smooth, and their diffraction patterns and general structure appears identical to bulk material, as shown by HR-TEM imaging and analysis of a flake milled at an angle. The excess material present at the edges of milled regions is shown to be crystalline, but its exact nature remains unknown. FIB-cut wires decreased in quality below approximately 150 nm in width. Smaller wires of good quality may be achievable, however, depending on the settings and characteristics of the FIB used to create them. Overall, FIB milling of Bi$_2$Se$_3$ is shown to have some limitations, but it remains a generally promising and easy method for manufacturing nanostructures.
TEM nanosculping of Bi$_2$Se$_3$ is also promising and addresses some of the drawbacks of the FIB milling method. Whereas FIB milling has at best 20 nm resolution and produces a large debris field at the edges of the cut regions, TEM nanosculping in the face-down configuration produces clean edges at sub-10 nm resolution. However, TEM nanosculpting of Bi$_2$Se$_3$ on SiN$_x$ windows comes with its own drawbacks. TEM sculpting takes considerably longer than FIB milling to produce nanostructures$^{42}$. Additionally, the 2010F did not have control software for automating the path of the probe beam or controlling exposure, so it was up to the user to determine what constituted “enough.” A combination of FIB and TEM milling techniques, however, is likely to provide a good compromise between convenience and ultimate resolution.

$^{42}$Many of my TEM drilling experiments ran overnight. FIB milling, on the other hand, took at most around 2 h.
Figure 3.26: HR-TEM and FFT of structures formed during face-up drilling that show unusual imaging behavior. In (a), the area boxed in violet shows the typical expanded hexagonal lattice and some unusual lattice planes. Its FFT in (b) shows the spots associated with these fringes (teal circles) and the expanded hexagonal lattice (dark pink circles). The image shown in (c), taken moments later, shows the same structure but with an unusual masonry-like lattice. Its FFT, shown in (d), shows what appears to be a body-centered cubic lattice viewed down the [012] zone axis (violet, gold, and berry circles), as well as the expanded hexagonal lattice (dark pink circles).

Another limitation of the Bi$_2$Se$_3$ TEM sculpting method on SiN$_x$ windows is the formation of redeposited and highly-resistant structures during the drilling process if the sample faces towards the beam direction. While this problem can be solved simply by flipping the sample upside-down, this requirement does limit the ability to perform in situ transport experiments. Transport holders typically require soldering, clamping, or wirebonding to contact pads, so making contact to them without advanced substrate features such as through-silicon vias is impossible. It is possible that producing suspended samples of Bi$_2$Se$_3$ would resolve this issue, but that method also brings its own complications. Regardless, for non-in situ experiments, TEM nanosculpting is a very useful tool in the arsenal of top-down fabrication methods for production of advanced topologically-insulating
devices with custom geometries.

3.5. Bismuth Selenide Alloying

3.5.1. Introduction

Topological insulators proximitized by superconductors, known as topological superconductors, are predicted to be capable of hosting Majorana fermions\textsuperscript{5,42}, which may be useful as the foundation for fault-tolerant topological quantum computing\textsuperscript{6,39}. While some evidence of topological superconductivity has been found in doped bulk topological insulators\textsuperscript{73–79}, and Majorana fermions have been reported in one-dimensional systems proximatized by superconductors\textsuperscript{80–83}, one of the remaining challenges in 2017 was to find a convenient experimental platform for creating circuits that could allow the pairwise “braiding” operations that form the foundation of topological quantum computing\textsuperscript{6}.

Bi$_2$Se$_3$ has been shown to become superconducting when doped with copper or other metallic elements\textsuperscript{73,76,78}, and Cu-doped Bi$_2$Se$_3$ has additionally been predicted to also exhibit topological properties\textsuperscript{84} and reported thus in some experiments\textsuperscript{77–79}. However, other experiments have reported that Cu-doped Bi$_2$Se$_3$ instead behaves as a conventional superconductor\textsuperscript{85,86}. This apparent conflict was resolved by the finding that Cu-doped Bi$_2$Se$_3$’s stability and electronic properties strongly depend on the growth and quenching conditions\textsuperscript{87}.

An alternative to the finicky doping process for producing topological superconductivity is to instead induce superconductivity in the Bi$_2$Se$_3$ surface states via the proximity effect from a nearby conventional superconductor\textsuperscript{88–91}. Both this and the doping techniques are very useful methods for studying the nature of topological superconductivity via spectroscopy, but complex device architectures and difficulties with establishing good contact with electrodes meant that in 2017, studying and harnessing topological superconductivity via transport measurements remained a significant challenge\textsuperscript{15}.

However, a fortuitous voltage-pulse \textit{in situ} anneal\textsuperscript{43} opened the door to a method that had the potential to combine the doping and proximity methods and direct-write superconducting regions into a superconducting crystal. It was found that palladium deposited via electron-beam lithography
and subsequently annealed either *in situ*\textsuperscript{44} or *ex situ* in a CVD furnace was absorbed into the Bi$_2$Se$_3$ crystal and began to exhibit superconducting behavior. Not only did this new technique dramatically improve the ability to make electrical contact to the sample, it also created a uniquely intimate and customizable interface between topologically insulating and superconducting regions that may lend itself well to the production of application-ready transport devices\textsuperscript{15}. Within this context, my aim was to determine the nature of the superconducting regions via TEM-based materials analysis.

Inspired by these results, I additionally sought to identify other transition metals that might react similarly with Bi$_2$Se$_3$ and could yield interesting results, what temperatures were ideal for these reactions, and what impact the reactions might have on transport phenomena. The metals I tested were niobium, due to its superconductivity; iron, due to its ferromagnetism; nickel, due to both its ferromagnetism and its presence in the same group of the periodic table as palladium; and tungsten, on a whim.

### 3.5.2. Experimental Methods

For these experiments, Bi$_2$Se$_3$ crystals of thicknesses between 70 nm to 100 nm were mechanically exfoliated onto 300 nm SiO$_2$ on (100) Si substrates or 100 nm-thick SiN$_x$ TEM windows using the methods described in Section 3.3.1. For the PdBi$_2$Se$_3$ experiments, palladium leads were patterned and deposited onto the flakes using the electron beam lithography methods described in Section 2.1.2 or using standard optical lithography methods by collaborators at Johns Hopkins University. After deposition and liftoff, samples were annealed in a quartz tube furnace at a set temperature between 200 $^\circ$C to 300 $^\circ$C under flowing argon gas at a rate of 200 sccm. The set temperature was maintained for 1 h, after which the tube furnace was turned off and allowed to cool naturally. For electrical measurements, a second layer of Pd leads was then added over the alloyed areas in order to reestablish good contact, as the annealing step could break the initial electrodes. TEM measurements were performed in the JEOL 2010F HRTEM. Raman spectra were measured using a backscattering geometry in a Horiba Join-Yvon T64000 spectrometer equipped with an Olympus microscope by collaborators at Johns Hopkins University. The 514.5 nm line of an Ar$^+$ laser was used for excitation, and the power was kept below 1 mW to avoid overheating and damaging the sample. The laser probe itself was about 2 $\mu$m in diameter, and the spectral resolution for the measurements was 2.5 cm$^{-1}$.

\textsuperscript{44}See Footnote 43.
Alloying experiments with iron, nickel, niobium, and tungsten were first performed by exfoliating Bi$_2$Se$_3$ flakes onto pre-deposited metal thin films using the parameters shown in Table 3.1 and then annealed to the specified temperatures in the quartz tube furnace using the same procedure outlined for alloying Pd with Bi$_2$Se$_3$ above. These samples were then inspected optically for evidence of a reaction. The thickness of the nickel films was also measured with the Bruker Dimension Icon AFM operated in tapping mode in order to determine the sputter rate. For TEM experiments, exfoliated flakes were positioned on 100 nm-thick SiN$_x$ windows using the PMMA transfer procedure described in Mlack et al.\textsuperscript{23}. 50 nm-thick Ni wires were then deposited onto these flakes, and TEM analysis was performed before and after annealing steps.

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Table 3.1: Sputtering parameters for deposited metals in the Singh Center’s Kurt J. Lesker PVD 75 PRO-Line Sputterer.

### 3.5.3. Palladium Bismuth Selenide Results

For transport measurements, Bi$_2$Se$_3$ nanocrystals of thicknesses between 70 nm to 100 nm were mechanically exfoliated onto silicon substrates, and Pd leads were patterned and deposited onto the nanocrystals using standard optical and electron-beam lithographic techniques. Without annealing, Bi$_2$Se$_3$ devices with Pd leads were metallic down to 0.25 K, as neither pure palladium nor bismuth selenide are superconducting materials. Devices were then annealed at a temperature of 200°C to 300°C. A device annealed at 220°C is shown in Fig. 3.27(a). After the annealing step, the 100 nm-thick Pd leads vanish from the surface of the Bi$_2$Se$_3$ crystal but remain intact elsewhere on the substrate. A second layer of palladium was then deposited over the former site of the first wires to reestablish good contact for electrical measurements. After the annealing step, a superconducting transition was observed at approximately 0.8 K.

A four-probe measurement of the resistance between leads 2 and 3 is shown in Fig. 3.27(b). A sharp
Figure 3.27: Electrical measurements of a Pd Bi$_2$Se$_3$ device after annealing in flowing argon at 220°C for 1 h. (a) Optical microscope image of the sample after annealing. Palladium leads are marked 1 to 6. The darker areas of the Bi$_2$Se$_3$ are where Pd was deposited on the flake and subsequently absorbed. (b) Four-probe resistance measurement vs. temperature with current applied across leads 1 and 6 and voltage measured across leads 2 and 3. (c) Four-probe V-I curve with current applied across leads 1 and 6 and voltage measured across leads 2 and 5. (d) Four-probe differential resistance measurements with current applied across leads 1 and 6. Voltage is measured across leads 2 and 5 (red), 2 and 3 (green, R1), 3 and 4 (blue, R2), and 4 and 5 (purple, R3). All 3 regions show transitions at slightly different bias currents. (e) Differential resistance measurements as a function of perpendicular magnetic field, with current applied across leads 1 and 6, and voltage measured across leads 2 and 5. (f) Differential resistance measurements as a function of temperature, with current applied across leads 1 and 6 and voltage measured across leads 2 and 5. In (e) and (f), primary peaks are observed at 2.5 µA and 3.5 µA.

Transition to a low but nonzero state can be seen at 0.8 K. Nonzero resistance is not a trait that superconductors possess, but this result arises because only part of the region between leads 2 and 3 is superconducting: in Fig. 3.27(a), a strip of light gray can be seen between leads 2 and 3, which indicates the absence of palladium within the Bi$_2$Se$_3$ crystal in that area. The I-V measurement across the entire device, seen in Fig. 3.27(c), shows a distinct nonlinearity at approximately 2 µA, which is emphasized by the differential resistance measurements across different parts of the device shown in Fig. 3.27(d).

Magnetic field-dependence and temperature-dependence of the differential resistance across the entire device are presented in Fig. 3.27(e) and (f), respectively. When either the temperature or the field is increased, the sharp decrease in resistivity at low currents gradually disappears in a way that
corresponds to a critical field of around 0.2 T. In both Fig. 3.27(e) and (f), two primary peaks are observed at 2.5 µA and 3.5 µA. Similar behavior of dV/dI has previously been reported in Bi$_2$Se$_3$ crystals with surface superconductivity induced by the proximity effect$^{89,90}$. Because palladium itself is not a superconductor, the observed superconductivity must be due to a product of the reaction that occurs during annealing.

Figure 3.28: Optical images and EDS spectra of exfoliated Bi$_2$Se$_3$ flake before and after thermal annealing with deposited palladium wires. (a) Optical image of Bi$_2$Se$_3$ flakes exfoliated onto SiN$_x$ windows and covered with lines of Pd. (b) TEM phase-contrast image of a Bi$_2$Se$_3$ flake with deposited Pd on its surface. This flake corresponds to the flake circled in red in (a). (c) EDS spectrum of red-circled area in (b), showing contributions from the Bi$_2$Se$_3$ flake and the SiN$_x$ window, but not Pd. (d) Optical image of the window after thermal annealing under flowing argon at 295°C for 1 h. (e) TEM phase contrast image of the red-circled flake in (d), also post-anneal. (f) EDS spectrum of red-circled area in (d), showing that Pd has seeped into the flake and spread from its original location.

In order to investigate the results of the reaction between Pd and Bi$_2$Se$_3$ during annealing, I imaged flakes exfoliated onto 100 nm-thick SiN$_x$ windows with deposited 90 nm thick Pd lines in the TEM before and after annealing for 1 h at 295°C under argon gas flowing at 200 sccm, with results shown in Figs. 3.28 to 3.30. Fig. 3.28(a) shows an optical microscope image of the sample before annealing. A phase-contrast image of the flake chosen for analysis (circled in red in Fig. 3.28(a)) is shown in Fig. 3.28(b). Additionally, the EDS spectrum of the red-circled region in Fig. 3.28(b) is shown in Fig. 3.28(c). The EDS spectrum indicates that, before the annealing step, the main elements present
in the region between the Pd lines are bismuth, selenium, and silicon from the substrate\textsuperscript{45}.

Fig. 3.28(d-f) show the same flake after the annealing step described above. It is clear in the optical image (Fig. 3.28(d)) that the parts of the flake in contact with the deposited Pd have changed in color to a distinctly darker gray. Similarly, a dramatic change can be seen in the phase-contrast TEM image shown in Fig. 3.28(e). Whereas the Pd lines were previously sharp, well-defined, and distinct from the Bi\textsubscript{2}Se\textsubscript{3} flake, they have vanished after the annealing step in favor of large, rounded dark patches. This result strongly suggests that the deposited metal has indeed been absorbed by the Bi\textsubscript{2}Se\textsubscript{3} crystal. This suspicion is borne out by the EDS spectrum of the central region of the flake shown in Fig. 3.28(e). Whereas palladium was initially absent from this region, a peak corresponding to the Pd L\textsubscript{α} line now appears in the EDS spectrum, indicating that not only has the metal been absorbed, but that it has also travelled somewhat through the material.

Figure 3.29: Elemental EDS maps of the annealed Bi\textsubscript{2}Se\textsubscript{3} flake shown in Fig. 3.28(e) and atomic ratios across the cross-section of the flake. (a) Counts-per-second image of the annealed flake. (b) EDS map of the bismuth M\textsubscript{α} line. (c) EDS map of the selenium L\textsubscript{α} line. (d) EDS map of the palladium L\textsubscript{α} line. (e) Atomic ratios of Bi:Se (red), Pd:Bi (blue), Pd:Se (green) across the cross section of the flake, starting with position 1 in the lower left-hand corner of the inset, and ending with position 6 in the upper right-hand corner of the inset.

To better understand the dynamics and extent of the Pd migration in Bi\textsubscript{2}Se\textsubscript{3}, I also took EDS maps of the flake shown in Fig. 3.28 after annealing. These spatial maps are shown in Fig. 3.29. Bismuth (Fig. 3.29(b)), and selenium (Fig. 3.29(c)) peaks are clearly present across the entire flake, however

\textsuperscript{45}Nitrogen has a fairly weak signal at 0.392 keV that is perhaps somewhat visible in the graph but was not analyzed.
the Pd signal (Fig. 3.29(d)) only a certain distance inwards from the original Pd lines and leaves an unaltered strip of Bi$_2$Se$_3$ in the center. The diminished intensity of the Pd L$_\alpha$ line at the border between the palladium lines and the flake, which is visible as a dark outline, suggests that the Pd atoms are pulled inwards from the lines into the flake during annealing until either the supply is exhausted (indicated by the break between the lines and the flake) or a certain concentration is reached.

The atomic ratios of Bi:Se, Pd:Bi, and Pd:Se were determined along a line profile (point scan area 0.04 $\mu$m$^2$), as shown in Fig. 3.29(e). The ratios of Pd:Bi and Pd:Se both decrease sharply in the central region, as expected based on the other EDS maps and scans indicating that Pd is absent from this region. The Bi:Se ratio, on the other hand, remained roughly constant across the entire flake at a value somewhat above 0.7 (or 2:3 at one significant digit). That is, the selenium concentration was measured as slightly less than expected. While the semiquantitative nature of EDS analysis without a known standard to work from may be partly at fault here, it is also reasonably likely that some selenium loss occurred during the annealing step. Despite stoichiometric Bi$_2$Se$_3$’s status as a topological insulator, which by definition indicates a bulk bandgap, commonly-occurring Bi$_2$Se$_3$ typically possesses metallic properties in the bulk due to selenium vacancies like the ones we may have observed. The effects of these vacancies can be mitigated through growth methods, chemical doping, or electrostatic doping.

I then attempted to get a better idea of what precisely the palladium was doing inside the Bi$_2$Se$_3$ using selected area electron diffraction. SAED patterns were taken at three different locations in the flake, which are circled in red in Fig. 3.30(a). The diffraction pattern in region 1, which EDS analysis showed to be an area free of palladium, is shown in Fig. 3.30(b). This pattern is consistent with that of Bi$_2$Se$_3$ when viewed down the [001] zone axis and shows a lattice constant of $a = 0.413$ nm. The diffraction patterns for regions 2 and 3, shown in Fig. 3.30(c) and (d) respectively, are considerably more complex. These regions apparently contain a plethora of crystal phases and orientations, as no sort of repeating pattern is apparent. The relatively constant Bi:Se ratio in these regions, however, suggests that the palladium atoms may be primarily disrupting the host lattice rather than replacing it.

Fig. 3.31 shows a phase-contrast image of a smaller and thinner flake on the same TEM window as the flake analyzed above using EDS as well as diffraction. This flake, which is centered vertically and
on the far left of the window in Fig. 3.28(d), appears completely gray in the optical image, and fairly dark in Fig. 3.31(a), where a number of distinct crystalline shapes can be seen in the flake away from the Pd lead. The SAED pattern shown in Fig. 3.31(b) confirms the appearance of the phase-contrast image in (a): the farthest point from the Pd line on the sample is massively polycrystalline and does not appear to show any sort of dominant phase or orientation. The SAED pattern from region 2 (Fig. 3.31(c)), which was directly atop where the Pd line was absorbed, however, shows a surprising amount of order compared to other regions analyzed that had a significant palladium load. In this image, a pattern with sixfold rotation symmetry still exists, although the pattern itself is split, with an offset of about 9.01° between the two primary sets of \{11\bar{2}0\} spots, with some streaking as well. This result indicates that the flake is twinned into at least two sub-crystals that are slightly misaligned and is also exhibits a large number of dislocations.\(^{94}\) It appears that that in this area
Figure 3.31: SAED analysis of a considerably thinner flake on the same window as the flake analyzed in Fig. 3.30. In (a), the red circles on the phase-contrast image indicate regions used for collecting diffraction patterns. (b) Diffraction pattern from region 1 in (a), far from the Pd lead. (c) Diffraction pattern from region 2 in (a), on top of the region where the Pd lead was absorbed. (d) Diffraction pattern of region 3 in (a), atop the Pd lead far from the Bi$_2$Se$_3$ flake.

the Bi$_2$Se$_3$ lattice has become distorted and swollen with palladium but has surprisingly not broken apart.

Overall, TEM analysis of the annealed flake shows definitively that the Pd leads are absorbed by the Bi$_2$Se$_3$ flake during the annealing process and that this absorption occurs uniformly with a leading edge across the flake. Although superconductivity has been previously reported in several compounds containing palladium, selenium, and optionally bismuth$^{95-97}$ transport data and TEM analysis do not conclusively show that such compounds are present in our samples.

By comparing the optical images with TEM and EDS data, we were also able to establish that it is quite simple to locate Pd-alloyed regions with only a light microscope: regions of a Bi$_2$Se$_3$ that
have been permeated with Pd appear dark gray rather than the shiny silver of natural Bi$_2$Se$_3$. In addition, comparing samples annealed at different temperatures yields the conclusion that the extent of Pd spread can be controlled by annealing temperature. At lower annealing temperatures, such as those used for the samples presented in Figs. 3.27 and 3.32, the absorbed Pd remains only in the targeted areas, whereas the flakes annealed to higher temperatures, such as the ones analyzed in Figs. 3.28 to 3.31, exhibit considerably more spread throughout the samples. Additionally, repeated measurements over the span of several weeks indicated that these samples do not degrade with time, and that the alloyed Pd remains in place.

Figure 3.32: Raman spectroscopy of Pd-alloyed exfoliated Bi$_2$Se$_3$ flakes on SiO$_2$. (a) Optical images of the Bi$_2$Se$_3$ flake (light gray) with an absorbed 90 nm Pd strip in the middle (dark gray). The bright spot in each image indicates the position of the Raman laser. Position 1 is far from the Pd strip; Position 2 is atop the Pd strip; Position 3 is to the left of the Pd strip; and Position 4 is to the immediate right of the Pd strip. (b) Raman scattering spectra of positions 1 to 4 within the range of Bi$_2$Se$_3$ phonon peaks. Spectra from positions 1, 3 and 4 show peaks that agree with measurements of pure Bi$_2$Se$_3$. The spectrum for Position 2 has no peaks because the Pd layer atop the Bi$_2$Se$_3$ is opaque to 514 nm-wavelength light.

Further evidence that the Bi$_2$Se$_3$ crystal structure remains intact far from the alloyed regions is provided by Raman spectroscopy. Fig. 3.32 presents Raman spectra taken on a Bi$_2$Se$_3$ flake annealed to 200°C in flowing argon with a small strip of Pd deposited along its center. Spectra were taken about 5 µm away from the Pd line (position 1), directly atop the Pd line (position 2), and directly to the left and right of the Pd line (positions 3 and 4). The spectra from positions 1, 3 and 4 all show phonon bands at 73 cm$^{-1}$, 132 cm$^{-1}$ and 176 cm$^{-1}$, all of which are typical of Bi$_2$Se$_3$. The widths of these bands range from 5 cm$^{-1}$ to 8 cm$^{-1}$, which is also typical of bulk Bi$_2$Se$_3$. These
results support our conclusion from TEM analysis that the alloying process does not disrupt the crystal structure away from the reaction site. Raman bands are not observed in position 2, atop the Pd line because the metallic layer prevents propagation of the visible excitation light.

3.5.4. Nickel Bismuth Selenide

The first NiBi₂Se₃ experiments were performed with Bi₂Se₃ flakes exfoliated onto Ni thin films and then annealed. The first anneal was to 260°C for an hour and produced no visible reaction. Then, the same sample was annealed to 350°C, and the results, shown in Fig. 3.33(a-b), clearly indicate that a reaction has taken place. In several patches on the larger flakes, dark bluish-gray patches have appeared, and some of the smaller and thinner flakes have entirely changed color. This was confirmation enough to prepare a sample of Bi₂Se₃ with Ni wires for TEM analysis, shown in Fig. 3.33(c). Like the flakes on the Ni thin film, after annealing to 350°C, S00 shows a color and morphology change indicative of a reaction, as can be seen in Fig. 3.33(d).

![Figure 3.33: Optical images of (a, b) Bi₂Se₃ exfoliated onto deposited nickel films and of (c, d) transferred onto TEM windows and patterned with nickel wires before and after annealing to 350°C.](image)

TEM analysis confirmed the visual evidence of a reaction. Fig. 3.34(a-d) show bright-field, STEM, SAED, and NiLα EDS images of S00 before the annealing process. The flake itself is relatively thick and nonuniform, and diffraction analysis of the {1120} spots yields a lattice spacing of $a = 0.425$ nm. The EDS in Fig. 3.34(d) confirms that the nickel remains confined to the deposited strips.

After the 350°C anneal, S00 has changed dramatically. The bright-field image shown in Fig. 3.34(e) now shows considerably more nonuniformity, including the appearance of a asterisk (∗) shaped set of dark bands radiating from the approximate center of the flake. Other dark bands have also appeared.
Figure 3.34: TEM analysis of Bi$_2$Se$_3$ sample with 50 nm thick Ni wires annealed to 350 °C. (a) Bright-field TEM image of the flake prior to annealing (colorized). (b) STEM image of the flake prior to annealing. Red circle indicates the area selected for diffraction analysis. (c) SAED pattern of the Bi$_2$Se$_3$ flake near a wire prior to annealing, with selected area inset. Wine circles indicate the ring of Bi$_2$Se$_3$ \{11\bar{2}0\} spots. (d) EDS map of the NiL$_\alpha$ line for the Bi$_2$Se$_3$ flake prior to annealing. (e) Bright-field TEM image of the Bi$_2$Se$_3$ flake after annealing at 350 °C (colorized). (f) STEM image of the Bi$_2$Se$_3$ flake after annealing. (g) SAED pattern of the Bi$_2$Se$_3$ flake near a wire after annealing. Wine circles indicate Bi$_2$Se$_3$ \{1\bar{1}20\} spots, the green circles indicate the previously invisible \{\bar{1}100\} first-order spots, and the teal arrows indicate some very small lattice spots that surround the second-order Bi$_2$Se$_3$ \{11\bar{2}0\} spots after annealing. (h) EDS map of the NiL$_\alpha$ line for the Bi$_2$Se$_3$ flake after annealing.

throughout the material, and the Ni wires are less uniform and smooth in appearance. The STEM image in Fig. 3.34(f) also shows several of the dark bands that were visible in the bright-field image, including the asterisk-shaped area and shows major disruption to the upper part of the flake and to the Ni wires themselves. The crystal structure as seen in the diffraction pattern has some changes (Fig. 3.34(g)): the first-order spots have become visible, as have some small faint spots that appear to be part of a hexagonal pattern that encircles the primary spots, although only up to two are visible for each primary spot in the pattern. The EDS pattern in Fig. 3.34(f) also firmly establishes that a reaction has taken place between the Bi$_2$Se$_3$ and the Ni wires, as it shows that the NiL$_\alpha$ signal now suffuses the flake, with its brightest areas being along the same defects that were visible in the bright-field and STEM images. Unlike palladium, which is soaked up by Bi$_2$Se$_3$ almost like water

As the reaction between the Bi$_2$Se$_3$ and Ni in S00 was both extensive and nonuniform, we then tried annealing a second flake with 50 nm nickel, S01, to 300 °C to determine if a lower reaction temperature limited the spread. The results of this lower-temperature anneal are shown in Fig. 3.35.
Fig. 3.35(a, b) present bright-field and dark-field images of the annealed Bi$_2$Se$_3$ flakes, which exhibit a large number of features that look like wrinkles along the directions of the lattice vectors. The STEM image shown in Fig. 3.35(c), however, shows only the vaguest indications of these wrinkles, unlike the very clear indications in Fig. 3.34. The Bi M$_\alpha$, Se L$_\alpha$, and Ni L$_\alpha$ maps of Fig. 3.35(d), however, still show that the nickel has broadly suffused into the Bi$_2$Se$_3$ flakes and does still appear to travel primarily along directions parallel to the lattice vectors. AFM maps of the flakes before and after the 350 °C anneal (Fig. 3.35(e) and (f), respectively), however, show that while the topography became somewhat more “patchy” after the annealing step, the flakes do not appear to have any major physical distortions as a result of the annealing process. Analysis of the diffraction pattern shown in Fig. 3.35(g), which unfortunately does not have visible {1010} spots, yields a lattice constant of $a = 0.424 \text{ nm}$.

Figure 3.35: TEM and AFM analysis of NiBi$_2$Se$_3$ Sample S01 after annealing to 300 °C. (a) Bright-field TEM images (stitched) of S01 after annealing, colorized. (b) Dark-field TEM images (stitched) of S01 after annealing, colorized. (c) STEM image of post-anneal S01, with red circle indicating area for SAED analysis. (d) EDS maps of post-anneal S01 for the Bi M$_\alpha$ peak (top left), Se L$_\alpha$ peak (bottom left), and Ni L$_\alpha$ peak (right). (e) AFM image of S01 prior to annealing. Blurry areas are loose nickel edges from liftoff. (f) AFM image of S01 after annealing. (g) SAED analysis of S01 after annealing. Wine circles indicate the ring of \{1120\} spots of Bi$_2$Se$_3$, and the teal circle indicates a twinned spot.

Though we were unable to prepare slices of this flake for cross-sectional TEM, we performed a somewhat similar experiment into the internal structure of the annealed flakes by taking them to
the FIB and thinning different areas of the sample to different extents. The beam current for this experiment was 10 pA, and the longest milling time was 15 s. Images from this experiment are shown in Fig. 3.36. Fig. 3.36(a) and (b) show bright-field and dark-field images of the Bi$_2$Se$_3$ flakes after the thinning process. Due to the large amount of missing material, these images are more difficult to read than their counterparts in Fig. 3.35, but by comparing the incompletely removed areas in the top right of the flakes, it can be seen that the thin material that remains does not contribute to the spot chosen for dark-field imagining. This is, however, not entirely surprising, as the process by definition introduces a large amount of damage to the lattice. The STEM image of the flakes is shown in Fig. 3.36(c), and it gives a somewhat clearer picture of the thinned areas of the flake. It is obvious that the FIB thinning did not occur evenly across the flake, which is a stark departure from the results of Section 3.4.

Figure 3.36: TEM and AFM analysis of NiBi$_2$Se$_3$ sample S01 after annealing to 300°C, then FIB thinning in nine regions. (a) Stitched bright-field TEM images of S01 after FIB thinning. (b) Stitched dark-field TEM of S01 after FIB thinning. (c) STEM image of post-FIB S01, with thinned areas boxed by dotted white lines and areas selected for diffraction analysis circled in red. (d) EDS maps of S01 after FIB thinning for the Bi M$_\alpha$ peak (top left), Se L$_\alpha$ peak (bottom left), and Ni L$_\alpha$ peak (right). (e) SAED for the upper circled area in (c), with selected area inset. Wine circles indicate the \{11\overline{2}0\} Bi$_2$Se$_3$ spots, and teal arrows indicate the new spots that appeared surrounding the primary diffraction spots after the annealing process. (f) SAED for the lower circled area in (c), with selected area inset. Wine circles indicate the Bi$_2$Se$_3$ \{11\overline{2}0\} diffraction spots, and the teal arrow indicates an auxiliary spot. (g) AFM image of S01 after annealing and FIB thinning.
The EDS maps of Fig. 3.36 provide clues about why this might be the case. Both bismuth and selenium are present in the incompletely milled areas, but more importantly, these areas also have large quantities of nickel. It is possible that the compound formed here is bound more tightly than $\text{Bi}_2\text{Se}_3$ and is therefore more able to resist high-energy gallium ion bombardment. Alternatively, this result could indicate only that because there was more material to remove in these areas, the material was not removed entirely. Fig. 3.36(e) and (f) show SAED images of the flake near a FIB-cut region and directly over a FIB-cut region that did not ablate Ni-rich regions, respectively. Analysis of both Fig. 3.36(e) and (f) both yield a lattice spacing of $a = 0.409 \text{ nm}$, which differs significantly from both S00 and the result from the diffraction pattern shown in Fig. 3.35(g) in that it undershoots the literature value of $0.414 \text{ nm}$ rather than overshooting it. The AFM topography in Fig. 3.36, meanwhile, shows that the preserved regions are not actually that much thinner than the surrounding non-ablated flakes, so it is not impossible for a compound to have formed that is more robust than $\text{Bi}_2\text{Se}_3$ alone.

![Figure 3.37: Analysis of change in $\text{Bi}_2\text{Se}_3$ sample S02 with annealing temperature.](image)

Next, we performed an annealing series with a new flake, S02, to investigate how annealing temperature affected a sample. The flake itself was about 100 nm thick and had 50 nm of Ni deposited atop in a central patch and across one corner. S02 was annealed first to 250°C, then 275°C, and finally to 300°C, with STEM images and EDS maps collected after each step. Fig. 3.37 shows the outcome of the experiment. Fig. 3.37(a-c) show STEM and NiL$_{\alpha}$ EDS maps for the flake at 250°C, 275°C and 300°C, respectively, and Fig. 3.37(d) shows an AFM scan of the flake before any annealing. At 250°C and 275°C, there is scant evidence of reaction in either the STEM or EDS images, but
a change is clearly visible in both STEM and EDS after the 300 °C anneal. While a faint signal is visible in the EDS after the first two anneals, the central patch of nickel becomes obviously marred after the third anneal, and bright patches in the EDS appear along the flake edges as well as along a new wrinkle in the lower right corner that is also visible in the STEM image.

Because the reaction at 300 °C was fairly subtle, we then prepared a new flake, S03, and annealed it to 325 °C to attempt to reach a compromise between the results of S02’s annealing and the extensive spread observed after S01’s anneal to 350 °C. Fig. 3.38 presents the results of that experiment, performed on a Bi$_2$Se$_3$ flake approximately 140 nm thick with, once again, about 50 nm of nickel deposited in a central patch and along one corner. In Fig. 3.38(a), the STEM image shows an asterisk-shaped pattern radiating from the central Ni patch, much like what appeared in S00. The diffraction pattern in Fig. 3.38(b) is from the corner of the sample beneath the Ni lead and shows both the pattern from the Bi$_2$Se$_3$ crystal as well as that of the polycrystalline nickel and indicates a lattice spacing $a = 0.403$ nm.

Figure 3.38: TEM and AFM analysis of NiBi$_2$Se$_3$ sample S03, annealed to 325 °C. (a) STEM image of S03 post-anneal, showing asterisk-shaped (∗) pattern radiating outwards from central nickel patch. (b) SAED image of lower left corner of S03, partially covered by Ni thin film post-anneal. wine-colored circles indicate Bi$_2$Se$_3$ \{1120\} spots, and green circles indicate the faint \{1100\} spots that appeared after the anneal. (c) AFM of S03 before annealing was performed. Blurry areas are due to loose edges on the Ni patches due to liftoff. (d) AFM of S03 after 325 °C anneal. (e) EDS of Ni L$_α$ peak of S03 after anneal, showing clear disruption of the central Ni patch and areas of high concentration throughout the sample. (f) AFM detail of the central Ni patch of S03. (g) EDS detail of the central Ni patch of S03, showing that areas of higher Ni concentration follow the asterisk symbol and appear to often follow lattice vectors.
AFM topography scans from before and after the annealing step are presented in Fig. 3.38(c, d, f) and show that unlike what was observed in S01, the topography does follow the wrinkles in the material post-anneal, and the EDS maps of the Ni L\textsubscript{α} line in Fig. 3.38(e, g) once again demonstrate that the visible wrinkles in the STEM image also correspond to nickel-enriched areas.

Figure 3.39: Diffraction, AFM, and EDS analysis of NiBi\textsubscript{2}Se\textsubscript{3} sample S04, annealed to 310 °C. (a) STEM images (stitched) of S04 after annealing. (b) SAED of gold-circled area in (a). Wine-colored circles indicate the \{11\overline{2}0\} diffraction spots of Bi\textsubscript{2}Se\textsubscript{3}, green-circled spots are the \{1\overline{1}00\} spots that seem to only become visible after annealing, and teal arrows indicate the small spots that surround the second-order Bi\textsubscript{2}Se\textsubscript{3} \{11\overline{2}0\} spots. (c) SAED of the -circled area in (a). In addition to the markings described in (b), the gold-circles indicate a new band of small, faint spots that appeared in this nickel-heavy region. (d) SAED of the teal-circled area in (a). Markings are as described in (b). (e) SAED of the green-circled area in (a). Markings are as described in (b). (f) SAED of the violet-circled area in (a). Markings are as described in (b), but the green spots have split considerably such that they form bands. (g) AFM topography of S04 post-anneal. (h) EDS map of the Ni L\textsubscript{α} line for S04. Colored circles indicate the same regions as in (a).

As the spread was still extensive and uncontrolled, one last sample, S04, was made from a 30 nm-thick flake with 50 nm of nickel deposited on top and then annealed to 310 °C. Fig. 3.39(a-f) shows a STEM image and diffraction analysis from across the sample. Fig. 3.39(c) and (f) specifically show
differences in their diffraction patterns. New bands of dots appear along the axes connecting the first-order spots. In Fig. 3.39(c), these may correspond to the appearance of a body-centered cubic or tetragonal phase, or they may be the result of an intercalated Ni layer, but they do not disrupt the first-order \{1100\} spots. On the other hand, the bands in Fig. 3.39(f) appear to be the result of splitting of the first-order spots, as the spots themselves occupy the same areas that one would typically find the \{1100\} spots. In the AFM topography scan shown in Fig. 3.39(g) the outlines of the wrinkles visible in the STEM image are subtler than in Fig. 3.38 but nonetheless present, and the Ni\textsubscript{L\alpha} map in Fig. 3.39(h) demonstrates that once again, the Ni did not remain local to where it was deposited, but rather spread along defects and edges to the far corners of the flake.

Stitched EDS maps of the upper corner of S04 are presented in Fig. 3.40. In this more detailed view, it is easy to see that the wrinkles visible in the counts image (Fig. 3.40(a)) directly correspond to areas in which the bismuth M\textsubscript{\alpha} signal (Fig. 3.40(b)) is weaker and both the selenium L\textsubscript{\alpha} and nickel L\textsubscript{\alpha} signals (Fig. 3.40(c, d)) are stronger.

Figure 3.40: EDS analysis of upper tip of Bi\textsubscript{2}Se\textsubscript{3} sample S04 after \textdegreeCelsius\textsubscript{C} anneal. White arrows indicate a few features that are shared across all maps. (a) Total counts EDS image (stitched). (b) Bi M\textsubscript{\alpha} EDS map (stitched). (c) Se L\textsubscript{\alpha} EDS map (stitched). (d) Ni L\textsubscript{\alpha} EDS map (stitched).

Similar experiments with deposited iron, tungsten, and niobium were also initiated but were not explored in as great detail. While optical inspection of Bi\textsubscript{2}Se\textsubscript{3} exfoliated onto iron thin films and then annealed did seem to indicate that an alloying reaction took place, the propensity of the iron
thin films to rust extremely rapidly discouraged me from continuing the study, especially since nickel 
already had been shown to react with Bi$_2$Se$_3$ and does not form destructive oxides. Fig. 3.41 shows 
example images of Bi$_2$Se$_3$ exfoliated onto iron thin films before and after annealing.

Niobium, on the other hand, had no evidence of a reaction with Bi$_2$Se$_3$ even up to 450°C, at which 
point higher temperatures became moot because the Bi$_2$Se$_3$ was profoundly damaged. The results 
of high-temperature annealing can be seen in Fig. 3.42. In Fig. 3.42(a), a phase-contrast image of 
the Bi$_2$Se$_3$ flake with deposited Nb strips can be seen—the flake itself is highly fragmented as if it 
had been shattered and put back together, but the Nb strips seem largely unaffected by the process. 
Fig. 3.42(b-c), which show before/after optical images of Bi$_2$Se$_3$ flakes on a 50 nm Nb film annealed 
to 300°C. No color change on the flakes can be seen, which suggests that no reaction had taken 
place.

Fig. 3.42(d) shows a SAED pattern from region 1 in (a), and the angles and spacing ratios for the 
diffraction spots match those of a body-centered cubic (bcc) crystal when nearly viewed down the 
[012] zone axis with a lattice parameter $a = 0.443$ nm. Fig. 3.42(e-f) show the SAED pattern and an 
HR-TEM image with FFT inset from region 2 in (a), which maintains its six-fold rotation symmetry 
and corresponds to a hexagonal crystal when viewed down the [001] zone axis with a lattice spacing 
$a = 0.422$ nm, which agrees well with the literature value of $a = 0.41$ nm $- 0.415$ nm$^{68}$. Fig. 3.42(g-h) 
show a SAED pattern and HR-TEM from region 3 in (a). These images suggest a cubic structure 
viewed down the [001] zone axis, and analysis reveals a lattice spacing of $a = 0.409$ nm. When the 
patterns from Fig. 3.42(d, g) are combined and analyzed as different angles on the same type of 
body-centered tetragonal crystal, lattice parameters $a$ and $c$ are found to be 0.407 nm and 0.403 nm, 
respectively, which in turn suggests that the crystals that form are actually body-centered cubic.

Tungsten similarly showed no evidence of a reaction with Bi$_2$Se$_3$ until the point of destruction.
Figure 3.42: Optical and TEM microscopy of Bi$_2$Se$_3$ annealed with niobium. (a) Low-magnification TEM image of Bi$_2$Se$_3$ flake annealed to 450 °C with Nb leads. (b) Optical images (100x) of Bi$_2$Se$_3$ exfoliated onto 50 nm Nb film before annealing. (c) 100x image of same sample as (b) after 300 °C anneal, showing no discoloration of the Bi$_2$Se$_3$ flakes. (d) SAED pattern of region 1 in (a), with selected area inset. The violet circle indicates the {200} spots, the gold circles indicate the {121} spots, and the dark pink circle indicates the {042} spot of a bcc lattice viewed down the [012] zone axis. (e) SAED pattern of region 2 in (a), with selected area inset. Green circles indicate the Bi$_2$Se$_3$ {1100} spots, wine circles indicate the Bi$_2$Se$_3$ {1120} spots, the teal arrows indicate new structure that appears around the primary spots, and the gold circles indicate additional faint lines of spots that appear between the primary second-order spots. (f) HR-TEM pattern of area that retains six-fold rotation symmetry, with FFT inset. In the FFT, the wine circles indicate the {1120} Bi$_2$Se$_3$ spots. (g) SAED of region 3 in (a), with selected area inset. The violet circles indicate the {200} spots, and the light blue circles indicate the {110} spots of a cubic or tetragonal lattice viewed down the [001] zone axis. (h) HR-TEM of area that exhibits four-fold rotation symmetry, with FFT inset. The violet and light blue circles indicate the same spots as in (g).
3.5.5. Discussion/conclusions

By a fortuitous accident, it was found that when metallic palladium is annealed with bismuth selenide, the result is a superconductor with a critical temperature of about $0.8 \text{K}$. This result may have important ramifications for applications of topological insulators such as topological quantum computing using Majorana fermions: the annealing process is guaranteed to produce an extremely close interface between the superconducting and normally topologically insulating regions, as the two are fashioned from the same initial crystal. In addition, we determined that both annealing temperature and flake thickness are important factors for determining the extent of palladium spread throughout the material, but for thick flakes and annealing temperatures around $220 \text{^\circ C}$, the alloyed region remains highly localized to the areas directly beneath the Pd patches. Therefore, superconductivity can be directly written into bismuth selenide crystals using simple e-beam lithography techniques. At higher temperatures, the Pd spreads considerably more through the Bi$_2$Se$_3$ flakes, which can be readily seen in both optical and TEM microscopy and was confirmed using EDS mapping. Diffraction data and Raman mapping prove after the annealing steps, regions free of palladium remain crystalline Bi$_2$Se$_3$ of good quality. Unfortunately, we were unable to determine what specifically in the alloyed region is superconducting, as the diffraction data largely showed that the lattice is either significantly disrupted or outright destroyed during the reaction to the point that in most cases, only a galaxy of spots with no apparent order can be seen. Future work on this finding may focus on the effects of even lower annealing temperature as well as structural characterization techniques that are able to probe a smaller sample volume than the selected area apertures on the 2010F TEM in order to find the mechanism behind the superconductivity and potentially produce devices with superconductivity direct-written into a Bi$_2$Se$_3$ crystal with sharper interfaces and less atomically jumbled material than we were able to obtain. Through this series of experiments, we were able to determine that nickel reacts extensively with bismuth selenide, but at a higher temperature than palladium and with markedly different spreading behavior. While the reaction between Pd and Bi$_2$Se$_3$ spreads along a roughly uniform front away from the Pd source during the annealing process, Ni appears to follow defects in the lattice, either ones that already existed in the flake, or ones it cleaves itself along the $\{1100\}$ planes. Additionally, its habit of spreading along the edges of the flakes make it difficult to confine to a single location, as significant concentrations of Ni can build up at locales quite distant from the initial reaction site. Diffraction patterns of the NiBi$_2$Se$_3$ flakes post annealing
show the appearance of new structures and patterns within a broader Bi$_2$Se$_3$ that remains relatively consistent, which is unlike the results of Pd Bi$_2$Se$_3$ flakes, which most typically show a complete fragmentation of the lattice in Pd-heavy areas. The diffraction patterns from Ni Bi$_2$Se$_3$ show many of the same features as those reported in Koski et al.\textsuperscript{99}, which suggests that zero-valent intercalation may be part of the reaction between nickel and bismuth selenide. Wide-scale intercalation may be the source for the wide-spread nonzero Ni L$_\alpha$ signal in the EDS maps of flakes post-annealing, including as low as 250 °C, as pre-anneal maps do not show the same sort of background. However, intercalation is likely not the only mechanism in play, as there is some evidence of a body-centered phase appearing in especially nickel-heavy regions, and EDS maps also show that the nickel-heavy regions are light in bismuth, indicating displacement. Regardless, annealing with nickel does not appear to produce a highly-localized reaction like palladium, so it may not be useful for introducing potential magnetism into carefully-controlled sites within a Bi$_2$Se$_3$ crystal, but the transport properties of the result may still be interesting. Cu–Bi$_2$Se$_3$, which is itself an intercalated compound, is known to be superconducting\textsuperscript{77–79}, and a nickel infusion may also prove to have unusual phenomena. It would be fruitful to conduct both cross-sectional TEM imaging and low-temperature transport measurements of Bi$_2$Se$_3$ flakes annealed with Ni patches at temperatures potentially even below 250 °C and for an extended period, to see if it is possible to isolate the potentially somewhat uniform intercalation reaction from the more significant and less predictable reaction that follows cleaving planes through the flake.

The results for our attempt at alloying Bi$_2$Se$_3$ with niobium were negative, but in an interesting way. After annealing a flake with deposited Nb wires to 450 °C, the flake appeared to fragment, and some of the fragments appeared to be body-centered cubic with a lattice constant of $a = 0.405$ nm, which is itself nearly the same as the lattice constant for hexagonal Bi$_2$Se$_3$ (0.41 nm to 0.415 nm\textsuperscript{68}). Bismuth itself is not body-centered cubic below 7.7 GPa\textsuperscript{100}, and Bi$_2$Se$_3$ only adopts a body-centered tetragonal structure above 30 GPa\textsuperscript{101}, so neither of these phases can be feasibly obtained inside a quartz tube furnace. γ-Bi$_2$O$_3$, while bcc, has a lattice parameter $a = 1.025$ nm\textsuperscript{102}, so I am unsure of the identity of whatever formed. The EDS maps shown in Fig. 3.43 confirm that whatever crystals did make their appearance after annealing, however, do not contain niobium as a substantive component.
Figure 3.43: EDS maps of the NbBi$_2$Se$_3$ flake annealed to 450 °C, showing (a) Bi M$_\alpha$, (b) Se L$_\alpha$, and (c) Nb L$_\alpha$. 
CHAPTER 4 : Vanadium Selenide Exfoliation and Materials Analysis

4.1. Background on Two-Dimensional Ferromagnets

Two-dimensional ferromagnetic materials research is an emerging and rapidly-growing field. In 1966, Mermin predicted that long range order was not possible in finite-size isotropic 2D Ising magnets, and from that point, it took about forty years to find examples of anisotropic 2D ferromagnets in the real world\(^\text{46}\). The first 2D ferromagnetic material\(^\text{47}\) was reported in 2006: Osada et al.\(^\text{104}\) found that nanosheets of Ti\(_0\cdot8\)Co\(_0\cdot2\)O\(_2\) were ferromagnetic and that it had spin-orbit induced anisotropy. In 2012, Zhang et al.\(^\text{105}\) found that nanosheets of Co\(_9\)Se\(_8\) were both half-metallic and ferromagnetic, and in 2014, Chen et al.\(^\text{106}\) found that δ-feOOH nanosheets were ferromagnetic semiconductors with a 2.2 eV bandgap. However, references to two-dimensional ferromagnets in the literature remained sparse until 2017, when the discovery of monolayer ferromagnetism in both Cr\(_2\)Ge\(_2\)Te\(_6\) by Gong et al.\(^\text{107}\) and CrI\(_3\) by Huang et al.\(^\text{108}\) caused somewhat of a sensation in the condensed matter community and opened the door to more intense and widespread research.

These materials, which have magnetic moments normal to their layers, have a wide variety of applications. In spintronics, these materials might be used in place of any other z-aligned ferromagnet to improve miniaturization as well as potentially allow the development of transparent and flexible spintronic devices\(^\text{106}\). Beyond that, however, out-of-plane 2D ferromagnetic materials, particularly CrI\(_3\), have also been shown to be able to split the valley degeneracy of WSe\(_2\), which may help foster the development of miniaturized computation based on the valley pseudospin\(^\text{109}\). And, of course, because out-of-plane ferromagnetic materials by definition produce magnetic fields in the z direction, these materials can also interact with the surface states of topological insulators. Hou et al.\(^\text{110}\) have predicted that a heterojunction between CrI\(_3\) and Bi\(_2\)Se\(_3\) should be able to create spin splitting at the Dirac point of Bi\(_2\)Se\(_3\)’s surface states without completely destroying their desirable features.

In addition to these out-of-plane 2DFMs, a class of two-dimensional materials with in-plane magnetic moments has also been recently discovered. These materials, VX\(_2\) where X = S or Se, fall under the umbrella of transition metal dichalcogenides (TMDs). Before the early 2010s, VX\(_2\) crystals had

\(^{46}\)Of course, it did have to wait at least until 2004, when 2D materials themselves were shown to be physically real by Novoselov K. et al.\(^\text{103}\)

\(^{47}\)That I found.
garnered some interest for somewhat niche applications: VSe$_2$ has been studied for decades as a 3D charge density wave (CDW) material$^{111-115}$ with a thickness-dependent transition temperature typically around 110 K$^{116}$, and in bulk it demonstrates an unusual warped and nested Fermi surface$^{117}$. Meanwhile, VS$_2$ research also began in the 1970s, with studies into its ability to intercalate lithium$^{118}$. VS$_2$ was also put forward as a promising candidate for in-plane supercapacitors due to its high 2D conductivity$^{119}$. It is also known as a CDW material, but interestingly enough, it does not appear to demonstrate the same type of Fermi surface nesting as VSe$_2$$^{120}$.

Outside the realm of magnetism, VX$_2$ materials continued to garner interest for applications including moisture sensors$^{121}$, low work-function contact electrodes$^{122}$, edge emitters for field emission$^{123}$, catalysts for electrocatalytic hydrogen evolution reactions$^{124-128}$ and hydrogen peroxide decomposition$^{129}$, and battery electrodes$^{130-133}$.

Within the magnetism community, on the other hand, research began when Ma et al.$^{134}$ predicted that VX$_2$ should have ferromagnetic properties in the two-dimensional limit. Zhang et al.$^{135}$ expanded on this analysis just a few months later and not only supported the prediction that VS$_2$ in particular should be ferromagnetic in the monolayer limit, but also that the trigonal (T) phase of VS$_2$ would become unfavored relative to a hexagonal (H) phase. Furthermore, H–VS$_2$ was predicted to have a greater magnetic moment than T–VS$_2$$^{135}$. Experimental confirmation of ferromagnetic response followed close behind, with Gao et al.$^{136}$ testing VS$_2$ and Xu et al.$^{137}$ testing VSe$_2$. This work continued quietly, with relatively few articles published, until 2017. Even though predictions emerged in 2015 and 2016 that these materials are predicted to have desirably high Curie temperatures: slightly below room-temperature 292 K for VS$_2$ and an outstanding 472 K for VSe$_2$$^{138}$, and even though H–VS$_2$ was predicted to be either a semimetallic$^{139}$ or semiconductor$^{138,140}$ ferromagnet, and H–VSe$_2$ was predicted to be a semiconductor ferromagnet$^{138-140}$, these materials remained relatively unknown. It was only in 2017, when the aforementioned announcement of out-of-plane intrinsic ferromagnetic materials generated widespread and keen interest, that VX$_2$ nanomaterials also began to enter the spotlight.

Since then, researchers have come up with a wide variety of potential applications for these new in-plane 2D magnetic materials. Of course miniaturized spintronics are one such application$^{141-143}$, and due to its low work function and high conductivity, VS$_2$ has been proposed to be an electrode material for making contact to semiconducting transition metal dichalcogenides such as MoS$_2$.$^{133}$
Such electrodes would both have low contact resistance and provide strongly spin-polarized current to the contacted material. Beyond that, VSe$_2$’s broken time reversal and inversion symmetry give rise to intrinsic valley polarization that is strain-tunable, which is promising for valleytronic devices. The highly-accessible transition energy between 1T–VX$_2$ and 2H–VX$_2$ also potentially facilitates using these materials for novel phase-change devices. Recently, VSe$_2$ has even been used as a saturable absorber for a mode-locked laser. And, of course, VX$_2$ may have potential use in any class of spintronic device that incorporates laterally-magnetized components (see Section 1.2.2).

One reason why research into vanadium dichalcogenides may have been muted for so long is that they are somewhat notorious for their difficulty to grow in bulk and handle. Until more careful procedures had been developed using chemical vapor transport (CVT), bulk crystals tended to demonstrate vanadium enrichment, and growth of large monocrystals also presented a major challenge. In addition, VX$_2$ materials are known to be moisture-sensitive, which was used to positive effect by Feng et al. in the descriptively-titled paper “Giant Moisture Responsiveness of VS$_2$ Ultrathin Nanosheets for Novel Touchless Positioning Interface” (emphasis mine) but is more generally known to be a pain in the backside. Worse, these materials have a mixed record on air stability (e.g. Liu et al. reports stable VSe$_2$, whereas Yu et al. reports decidedly unstable VSe$_2$) that primarily depends on defect concentration. To add even more to the challenge, mechanically exfoliating VSe$_2$ using adhesive tape is extremely difficult due to relatively strong interlayer Van der Waals forces. Additionally, whether or not VX$_2$ materials are intrinsically ferromagnetic or if the observed magnetism is instead due to defects or lattice distortions due to strain or other factors. Different methods of calculating the energy structure have led to different results, and the difficulty of obtaining stoichiometrically pure VSe$_2$ has made a definitive experimental conclusion elusive. It is known that both strain and defects alter (and in the case of selenium vacancy defects, enhance) the ferromagnetic response, however.

Regardless, obtaining large-area monolayer VX$_2$ remains a necessary step towards both study into the properties and applications of these materials. Several avenues have been explored in efforts to attain monolayer VX$_2$, including molecular beam epitaxial (MBE) growth, mechanical exfoliation from bulk crystals, colloidal synthesis, hydrothermal synthesis, CVD growth, liquid phase exfoliation, and electro-
chemical exfoliation. This is indeed a broad suite of experimental techniques, and it behooves us as researchers to thoroughly investigate the benefits and drawbacks of each method so that we may translate simple characterization into facile, scalable, and quality device production under a variety of circumstances. In addition, it is important to consider various methods of improving environmental stability of these materials, e.g., through capping, encapsulation, or passivation.

In service to these goals, my research into VSe$_2$ has focused on exploring two different exfoliation techniques. The first technique I tried was mechanical exfoliation, expanding upon the method detailed by our VSe$_2$ source 2D Semiconductors by comparing success rates of different types of adhesive tape and experimenting with annealing temperatures for removing adhesive residues in a vacuum oven. Flakes were studied using AFM, MFM, and my newly-developed TR-MFM procedure. After determining the limits of my ability for this technique in the lab, I committed to fleshing out the details of both the preparation and environmental degradation of ultrathin 1T-VSe$_2$ obtained via electrochemical exfoliation and passivated with solutions of 1H, 1H, 2H, 2H-perfluorodecanethiol (FDT, C$_{10}$H$_5$F$_{17}$S), based upon the work of Yu et al. The structure and magnetic response of the resulting flakes were investigated using TEM down to cryogenic temperatures, EDS, AFM, MFM, and Raman spectroscopy. We found that when ultrathin VSe$_2$ flakes oxidize, the oxide forms small pillars on top of the flake.

Diluting passivation chemicals is a common technique for improving production economy, so we also explored the effects of FDT concentration in ethanol on passivation efficacy and sample cleanliness. We also demonstrated the suitability of VSe$_2$ ultrathin flakes for TEM nanosculpting and determined the end products of the solvent-mediated decomposition of VSe$_2$ in propylene carbonate.

4.2. Experimental Details

4.2.1. Mechanical Exfoliation

High-purity bulk VSe$_2$ was purchased from the manufacturer 2D Semiconductors and stored under vacuum until ready for use. Matte Scotch® Magic™ Tape (green-label), 1 Mil Kapton® polyamide tape, and 1 Mil low-residue blue poly tape were used for mechanical exfoliation. The procedure provided by 2D Semiconductors for mechanically exfoliating VSe$_2$ flakes is as follows:

Manufacturer unknown
1. Pre-clean a silicon wafer fragment with 285 nm to 300 nm-thick SiO$_2$ by soaking it in Piranha solution for one hour, rinsing in deionized water, drying with a nitrogen gun, and finally put through a plasma cleaning cycle.

2. Place a piece of bulk VSe$_2$ on the adhesive side of a strip of tape (Tape 1).

3. Gently place the adhesive side of a second strip of tape (Tape 2) on top of the adhesive side of Tape 1, and allow them to adhere. If necessary, gently press with gloved fingers.

4. Very slowly exfoliate the tapes from each other. Pull-apart rate should be approximately 1 mm/s. Tape 1 may be stored for later. It is also important to keep good tension on the tapes while exfoliating and also to minimize the angle between the two tapes as they are being pulled apart.

5. Take a third tape (Tape 3) and exfoliate it from Tape 2 using the same method. Tape 2 may be stored for later.

6. Apply tension to Tape 3, ensure that it is flat, and approach the clean SiO$_2$ wafer fragment with the tape. Then place the tape down. It should adhere right away.

7. Using the weight of your finger, press very lightly on Tape 3.

8. Exfoliate Tape 3 from the wafer very slowly, at about 0.5 mm/s. Maintain good tension on the tape. Ensure that the angle between the wafer and the tape is 10° to 30°.

After this exfoliation process, the SiO$_2$ wafer fragments were placed in gel boxes, which were then sealed in vacuum bags and shipped to Columbia University and annealed at $10 \times 10^{-7}$ Torr to remove adhesive residues. After shipping to the University of Pennsylvania, samples were then stored in a vacuum dessicator until ready for use. When analyzed, fragments were first inspected under a metallurgical microscope to determine if massive oxidation had occurred and to locate areas of interest, before mounting on magnetic AFM sample pucks and loading into the Bruker MultiMode 8 AFM. Topographic measurements were performed on mechanically-exfoliated VSe$_2$ flakes in ScanAsyst® mode.
4.2.2. Electrochemical Exfoliation

Following the procedure established by Yu et al., we prepared few-layer to monolayer samples of VSe₂ via electrochemical exfoliation. The electrolyte solution was composed of 5 mM of tetrapropylammonium chloride (TPrACl (CH₃CH₂CH₂)₄N(Cl), Sigma-Aldrich 98%) dissolved in anhydrous propylene carbonate (PC, C₄H₆O₃, Sigma-Aldrich 99.7%). The VSe₂ cathode was held in place by a bent strip of 0.127 mm-thick titanium foil (99.99+%, Alfa Aesar), and platinum wire (99.5%, Alfa Aesar) served as the anode. Reactions took place in a glass cuvette, as the PC/TPrACl solution was found to dissolve polymethyl methacrylate (PMMA) cuvettes. The cuvette was prevented from tipping over by a custom cage I designed and 3D printed from ABS plastic. To drive TprA⁺ ion intercalation and subsequent VSe₂ exfoliation, voltages between 2 V to 2.5 V were applied using a Yokogawa 7651 programmable DC source, with exfoliation of the flakes selected for study occurring at 2.5 V for 30 min. Fig. 4.1(a) shows the exfoliation setup, with an image of the CAD mockup inset. Fig. B.5 in Appendix B provides a detailed diagram for this part. The VSe₂ crystal was removed to a fresh solution of PC after visibly expanding and turning completely black (the black color can be seen in Fig. 4.1(a)). After manually shaking the resultant liquid until the flakes appeared well-dispersed and then sonicating for 1 min to 2 min, the black suspension (Fig. 4.1(b), top) was transferred to the argon glovebox and immediately drop cast.

Piranha-cleaned silicon wafer fragments coated with 300 nm of wet thermal silicon oxide (Fig. 4.1(c)) and fresh holey carbon grids were used as substrates for AFM/MFM measurements and TEM experiments, respectively. These samples were then immediately transferred to the vacuum antechamber of the glovebox to dry overnight, except in the case of the grid used for cryogenic TEM. The cryo-TEM grid was loaded into the Gatan ULTDT liquid helium TEM holder immediately after drop casting with the propylene carbonate-VSe₂ suspension and while still wet, then placed under high vacuum (10 × 10⁻⁶ Torr) overnight. For surface passivation, FDT (97%, Sigma-Aldrich) was used on its own as well as diluted to the following concentrations in ethanol: undiluted, 5 mM, and 3 mM. Control samples were treated with pure ethanol. All samples were immersed in their treatment solutions overnight and then washed with acetone. AFM/MFM samples were then quickly dried in air with a nitrogen gun before being returned to the argon glovebox, whereas TEM grids were allowed to dry evaporatively under argon. Immediately prior to AFM and MFM measurement, samples were immersed and gently agitated in isopropanol for ten minutes before blow drying with either a
nitrogen gun or canned air. The samples were then mounted on magnetic sample pucks using a strip of carbon tape. Before TEM measurements, grids were rinsed in methanol and dried under argon.

Figure 4.1: Exfoliation of ultrathin VSe$_2$: (a) Exfoliation setup, including 3D-printed cuvette holder (CAD inset), glass cuvette containing propylene carbonate, tetrapropylammonium chloride, platinum electrode, and titanium hook electrode holding bulk VSe$_2$ crystal. The crystal turns black when the intercalation process begins to separate individual layers. (b) Propylene carbonate containing suspended ultrathin VSe$_2$ flakes (top left), atomic structure of single 1T–VSe$_2$ unit cell (top right), and structure of three VSe$_2$ layers (bottom). (c) Optical image of exfoliated VSe$_2$ flakes drop cast onto Si/SiO$_2$ wafer fragment.

Atomic and magnetic force microscopy measurements were performed in air on successive days to determine the extent of ultrathin VSe$_2$ degradation in atmosphere over a span of approximately 24 hours. At the time of measurement, the exfoliated samples analyzed had been stored in the glovebox for four months. However, topography measurements on samples prepared from a new exfoliation and measured within the same week appeared similar. Topography measurements were taken using the ScanAsyst-HR mode. For MFM and TR-MFM measurements, Bruker MESPV2 tips were magnetized with a lateral field in the lab-built magnetizer (Fig. 4.2) for 5 to 10 min before being loaded into the AFM. For the first MFM scan, the magnetized tip was set to the highest lift height at which good contrast was achieved, and the scan taken the next day maintained that lift height, typically around 20 nm.
Figure 4.2: 3D printed tip and sample magnetizer and transfer arm. The magnetizer is printed from blue nylon, and the transfer arm is printed from black ABS plastic. The design of the magnetizer allows for a field either coplanar with the sample or MFM cantilever (as shown) or perpendicular to the material when tipped on its side. The 3” x 1/4” N45 sintered NdFeB magnets (13500 G, 70 lbs pulling force, CMS Magnetics) are super-glued in place to prevent them from flying off the printed base and sticking to both each other and any nearby ferrous metal and are labeled for safety.

TEM data were taken at 200 kV in the JEOL F200 microscope in bright-field, SAED, and STEM mode. EDS mapping and analysis were performed in Digital Micrograph.

Raman spectroscopy of the VSe$_2$ nanoflakes was performed under 785 nm laser excitation on both bare and 5 mM FDT-passivated flakes on Si/SiO$_2$ substrates. Spectroscopy was performed on the same samples that were used for the AFM and MFM time series and collected after the AFM and MFM measurements had taken place.
4.3. Results

4.3.1. Mechanical Exfoliation

The first mechanically exfoliated samples I made were vacuum-annealed to a temperature of 450 °C and were determined to have heavily oxidized during return shipping by the appearance of orange coloration under optical inspection. While flakes annealed to 350 °C initially appeared unoxidized, after about 30 min of study under an optical microscope, thicker flakes took on a decidedly orange cast, as can be seen in Fig. 4.3.

![Image of post-anneal oxidized VSe₂ at 50x magnification (scalebar unavailable). The orange color indicates the presence of VO₂.](image)

Fig. 4.4 shows an optical image and an AFM topography scan of the thinnest mechanically-exfoliated VSe₂ from my research, which has minimum thickness of approximately 5 nm. Fig. 4.4(a) is representative of the typical density of VSe₂ flakes I was able to obtain with either Scotch® tape or low-residue blue poly tape—Kapton® tape performed extremely poorly and covered the wafer fragments in adhesive residue without successfully exfoliating the flakes.
Figure 4.4: (a) Optical image of unannealed VSe$_2$ sample prepared by mechanical exfoliation. VSe$_2$ flakes can be seen primarily in the red circled region, but there is one blue-tinted silver flake in the upper right quadrant of the image, and a few thinner flakes at the bottom below the red circle. Other features are predominantly adhesive stains. Scale bar is 10 µm. (b) AFM image of the thinnest flake of mechanically-exfoliated VSe$_2$ located after many trials.

4.3.2. Electrochemical Exfoliation

Fig. 4.5 shows the results of topography scans for samples treated with (a) pure ethanol, (b) 3 mM FDT in ethanol, (c) 5 mM FDT in ethanol, and (d) pure FDT. Severe degradation of the control flake is apparent: only the very thickest parts of the flake remain intact, while the rest of the area has become a loose debris field overnight. Even during the first day of measurements, substantial debris from the control flake built up along the edges of the scanned region, which can be seen in the lower half of Fig. 4.5(a). The 3 mM FDT-treated sample shown in Fig. 4.5(b) also degraded substantially, with the “lacy” areas becoming lacier and a larger network of holes opening up in the thin flakes on the right side of the image. Additionally, the small bumps that can be seen on the flakes (red) grew larger. The 5 mM FDT-treated flakes showed less degradation in the pre-existing “lacy” areas with holes and smaller towers of what was presumed to be vanadium oxide, as can be seen in Fig. 4.5(c). In addition, the few-layer flakes did not decompose into a network of holes as the 3 mM flakes had. Finally, the sample treated with pure FDT (Fig. 4.5(d)) shows very little change over the span of 24 h, with only the appearance of small bumps similar to those seen on the 3 mM FDT-treated flakes from the outset observed as a noticeable difference. These regions were observed even after extremely brief periods in air and regardless of passivation technique. The working hypothesis for this result was that the damage accrued with time spent in the propylene carbonate suspension. Fig. 4.6 supports this conclusion, as the sample shown was dried using a more
powerful Edwards nXDS 6i scroll pump rather than the Edwards RV12F rotary vane pump used for the other samples. This choice of vacuum pump decreased both the drying time and the observed damage to the very thinnest flakes. Indeed, a monolayer region with relatively few holes can be seen in the lower left part of Fig. 4.6(a) and (b). These measurements also indicate that storage in the argon glovebox does not substantially degrade the VSe₂ samples, as can be seen most clearly by comparing the topography with the wide range of thicknesses observable in Fig. 4.5(a). No damage obviously in excess of what is apparent Fig. 4.6 can be seen.

Figure 4.5: AFM topography of electrochemically exfoliated VSe₂ flakes treated with (a) pure ethanol, (b) 3 mM FDT in ethanol, (c) 5 mM FDT in ethanol, and (d) pure FDT at roughly 0 h (top) and 24 h (bottom). Note that the scale is capped at 20 nm for consistency and visibility of the thinnest VSe₂ flakes.

Fig. 4.7 shows the same time series with MFM phase scans of the ethanol control, 5 mM FDT-passivated, and pure FDT-passivated samples. Initially, the control flake shows strong signal in the lacy monolayer areas and at high peaks in the scanned region. The main body of the flake and some of its surface features are readily distinguishable from background but are dwarfed by the monolayer lacy and high-peak areas. The main body of the flake is about 4 nm thick, which is the thickest we measured. Therefore, it should also be the flake with the weakest surface fields, as it is the closest to the bulk material. At the same settings, the MFM phase signal of the control flake decreased by about one order of magnitude after 24 h, and other than the large central patch that also remained in the topography, is nearly indistinguishable from background. The 5 mM FDT-treated sample in Fig. 4.7(b) shows that the observed topographical peaks, hypothesized to be oxidation, increase...
overnight in air but only locally suppress the magnetic response without affecting the rest of the flake. In addition, the surface fields from the lacelike degraded areas can be seen, strengthening our conclusion that while complete oxidation almost totally destroys the magnetic signal, more moderately damaged VSe$_2$ retains some virtue, consistent with the transport results presented by Yu et al.$^{154}$ Finally, in Fig. 4.7(c), we can see that there has also been little to no discernible degradation of the ferromagnetic signal, as expected since little to no damage was discernible in the topography.
Figure 4.7: MFM phase measurements of VSe$_2$ flakes treated with (a) pure ethanol, (b) 5 mM FDT in ethanol and (c) pure FDT at roughly 0 h (top) and 24 h (bottom). In (a), the features in the top quarter of the 24-hour image are not associated with any topography and are suspected to be spurious instrument fluctuations. In (c), note that after passing over a high feature in the approximate center of the first scan, the contrast inverted at the horizontal line. The contrast in the upper part of the image has been inverted back for easier viewing.

Fig. 4.8 shows topographical, TR-MFM, and MFM detail of a thicker and lower-quality bare exfoliated VSe$_2$ flake. While the material itself as well as the surrounding substrate are fairly strewn with debris or VSe$_2$ dust, and the substrate appears to have some solvent stains, it is still possible to get a clear magnetic signal. In both the TR-MFM and the zoomed-in MFM images, the appearance of phase contrast can be seen in the thinnest parts of the flake, with the distinction from background largely disappearing at the 15 to 20 nm mark.
In order to verify the structure of the exfoliated material, some of the VSe$_2$ suspension was immediately drop cast onto copper holey carbon grids. After drying, the bare VSe$_2$ grids were transported to the JEOL F200 TEM under argon and then quickly loaded into the TEM for atomic-resolution imaging. As can be seen in Fig. 4.9(a) and (b), the crystal structure of the flake has hexagonal symmetry, as one would expect from a trigonal (1T) or hexagonal (2H) lattice. Direct profile measurement of the bright-field images down the [001] axis yields a lattice constant of 0.337 nm, which compares favorably with the literature value of 0.336 nm measured using XRD$^{137}$. Fig. 4.9(c) shows a bright-field HR-TEM image of bare VSe$_2$ at 87.7 K, which has a smaller lattice spacing of 0.332 nm. The EDS spectrum shown in Fig. 4.9(d), meanwhile, shows the presence of vanadium, selenium, and potentially oxygen$^{49}$, as well as background carbon, copper, and zinc$^{50}$. Fig. 4.9(e) compares the

$^{49}$The oxygen K line and vanadium L-line substantially overlap and could not be resolved in these experiments.

$^{50}$In addition to the copper grid, some components of the TEM holder are made of either zinc or brass.
Raman spectra for thick and thin untreated VSe$_2$ flakes after approximately 24 hours of air exposure. The characteristic vibration peak appearing at 206 cm$^{-1}$ corresponds to the A$_{1g}$ mode of 1T VSe$_2$. The peaks at 236 cm$^{-1}$ and 249 cm$^{-1}$, meanwhile, indicate the presence of vanadium oxides, supporting the hypothesis that the “towers” appearing in the AFM topography correspond to oxide formation.

Figure 4.9: TEM and Raman analysis of bare electrochemically-exfoliated VSe$_2$ ultrathin flakes. (a) Room-temperature HR-TEM of suspended thin VSe$_2$ showing a lattice spacing of 0.337 nm. (b) Room-temperature selected-area electron diffraction of suspended thick VSe$_2$ with simulation inset. (c) 87.8 K HR-TEM image of suspended thin VSe$_2$ with a lattice spacing of 0.332 nm. (d) EDS spectrum of bare VSe$_2$ on holey carbon grid, showing vanadium and selenium as well as a miniscule sulfur peak, but no fluorine. (e) Raman spectra of thick (red) and thin (blue) bare VSe$_2$ flakes on Si/SiO$_2$ wafer fragment.

Fig. 4.10 shows HR-TEM images of VSe$_2$ flakes from the same grid as shown in Fig. 4.9 after approximately 12 h air exposure. The patchiness of the suspended flake in Fig. 4.10(a) contrasts dramatically with the inset image, which shows a freshly-prepared VSe$_2$ flake that was placed in the TEM directly without time to oxidize. The semi-oxidized region shown in Fig. 4.10(b) appears amorphous and exists primarily around complete holes in the material. Such holes in the VSe$_2$ flakes
arise from both air exposure and beam irradiation. In Fig. 4.10(c), a fortuitous “nanobridge” was located that, with a lattice constant of 0.45 nm, be composed of orthorhombic V$_2$O$_5$ \(^{164}\). It also proved possible to perform rudimentary nanosculpting of the VSe$_2$ flake in bright-field mode—the beam was brought to crossover and idled for a moment before re-spreading. Fig. 4.10(d) shows the result of this experiment: after brief and concentrated irradiation, a pore surrounded by an approximately 5 nm-thick amorphous region emerged. Beyond the amorphous band, the flake evidently remained 1T–VSe$_2$ with a lattice constant of 0.331 nm.

Similar material analysis was also performed on VSe$_2$ flakes treated with FDT, as shown in Fig. 4.11. The most defining feature of the FDT-treated samples during TEM analysis was extensive carbon contamination: the dark rings and fully black ovals that can be seen in Fig. 4.11(a) are due to carbon contamination on a grid, treated with pure FDT and then washed with acetone and isopropanol, from viewing the imaged region under higher magnification and STEM mode, respectively. Fig. 4.11(b) shows a SAED pattern from a sample treated with 5 mM FDT in ethanol, rinsed in acetone and isopropanol, and then run through a rapid thermal annealing (RTA) cycle at 350 °C to remove excess carbon. The RTA step permitted EDS spectrum collection without carbon contamination building up to the point that it heavily obscured the imaging region.

Despite the significant challenge, we were able to collect an HR-TEM image of the pure FDT-treated sample that had not undergone RTA—as shown in Fig. 4.11(c)—and obtained a lattice constant of \(a = 0.382\) nm. Fig. 4.11(d) shows the EDS spectrum results for the 5 mM FDT-treated and annealed flake. In addition to the previously detected elements, a noticeable fluorine K line appears, indicating the presence of the FDT fluorocarbon. The sulfur signal remains quite small—this is unsurprising due to the stoichiometry of the FDT molecule\(^{31}\). Fig. 4.11(e) compares the Raman spectra of bare VSe$_2$ flakes and 5 mM FDT-treated VSe$_2$ flakes. No shift in the A$_{1g}$ peak of VSe$_2$ was observed, but the peak appeared somewhat larger for the treated flakes. This difference may be attributed to differences in flake thickness. Fig. 4.12 expands on the extent of carbon contamination of un-annealed FDT-treated flakes. Fig. 4.12(a-f) show EDS maps of Fig. 4.12(a) the EDS sum signal and Fig. 4.12(b-f) the primary elements found in the sample. Fig. 4.12(g) shows the EDS spectrum for this sample, where it is clear that the carbon peak towers over all the rest.

In order to further investigate the effects of extended exposure to propylene carbonate on VSe$_2$, \(^{31}\)That is, 10 carbon atoms, 5 hydrogen atoms, seventeen fluorine atoms, and one lonely sulfur.
Figure 4.10: Oxidation damage and both naturally-occurring and deliberately-sculpted structures appearing in bare VSe$_2$ with approximately 12 h air exposure. (a) Low-magnification image of air-exposed VSe$_2$ flake over carbon grid. Bare, unoxidized flake shown in inset for comparison. (b) HR-TEM image of oxidized region adjacent to crystalline VSe$_2$. Crystalline region has lattice spacing of 0.35 nm. (c) “Nanobridge” found in damaged region of air-exposed VSe$_2$, showing a lattice spacing of 0.45 nm. (e) Edge of a pore drilled by rapidly bringing the beam to crossover in bright-field TEM mode. There is approximately 5 nm of amorphous material between the pore itself and crystalline hexagonally-symmetric VSe$_2$ with a lattice spacing of 0.31 nm.
Figure 4.11: Analysis of passivated VSe$_2$. (a) Phase-contrast TEM of suspended VSe$_2$ treated with pure FDT. Extensive carbon contamination can be seen from higher-magnification imaging (dark circles), STEM spot mode (black ovals), and beam damage. (b) SAED pattern of 5 mM FDT-treated thin VSe$_2$ flake. (c) HR-TEM image of suspended VSe$_2$ flake treated with pure FDT. Amorphous regions due to carbon contamination of the surface are abundant, but it is possible to obtain a lattice spacing of 0.382 nm from non-covered areas of the sample. (d) EDS spectrum of 5 mM FDT-treated sample post RTA, showing vanadium, selenium, potentially oxygen (O K cannot be resolved from V L), as well as small fluorine and sulfur peaks. (e) comparison of bare (red) and 5 mM FDT-treated (blue) VSe$_2$ Raman spectra.

we prepared a holey carbon TEM grid with electrochemically exfoliated VSe$_2$ that had spent 48 hours in propylene carbonate suspension post-exfoliation. Fewer VSe$_2$ flakes were observed than in younger suspensions, and those that were found appeared thicker in the electron microscope, were often damaged, and had high sensitivity to further beam damage. Fig. 4.13(a, c) show one such flake, as well as its propensity for continuing damage. HR-TEM images obtained from these flakes (Fig. 4.13(b)) nonetheless demonstrated a lattice spacing of 0.336 nm, which remains consistent with both our previous results and the published value for VSe$_2$. EDS mapping, presented in Fig. 4.13(d), also shows considerably less selenium present than in either the fresh unpassivated or the fresh passivated flake, which indicates a very high number of selenium vacancy defects.
Figure 4.12: (a-f) EDS mapping of unannealed VSe$_2$ flake treated with 5 mM FDT in ethanol. (g) EDS spectrum of the same flake, demonstrating the extensive carbon contamination compared to the signal from the VSe$_2$ flake.
Figure 4.13: TEM and EDS of VSe$_2$ from 2-day-old solution. (a) Low-magnification image of VSe$_2$, showing the beginnings of a tear. (b) HR-TEM image of aged VSe$_2$, showing a lattice spacing of 0.336 nm. (c) HR-TEM image of the edge of the tear in the VSe$_2$ flake, which continued to expand quickly during imaging. (d) EDS spectrum of aged VSe$_2$ flake, showing carbon, oxygen, vanadium, and selenium.

However, these damaged flakes were not the only solids to appear in the aged solution. Both rectangularly-symmetric nanowires and highly-porous “chunks” with a network of circular holes were found on the same grid. Fig. 4.14 shows TEM and EDS analysis of a few of the nanowires and chunks. It can be seen in Fig. 4.14(a) that the nanowires are numerous, rectangular in shape, and can be several microns in length. The HR-TEM image in Fig. 4.14(b) and its associated FFT in Fig. 4.14(c) confirm the rectangular symmetry, and a lattice spacing of 0.45 nm is observed. This measurement agrees with published values for selenium nanowires$^{165}$. Our hypothesis that the rectangular crystals are primarily elemental selenium gains support from the EDS maps shown in Fig. 4.14(d-f). The vanadium in the region of the nanowire is suppressed, while the selenium signal is atypically strong, as one would expect from a selenium crystal perched atop a damaged VSe$_2$ flake. The precipitation of selenium nanowires would also explain the disappearance of the selenium signal from the EDS in Fig. 4.13.
Conversely, for the chunk shown in Fig. 4.14(g), the vanadium EDS signal is powerfully enhanced (Fig. 4.14(h)), and the selenium signal (Fig. 4.14(i)) is quite weak, which is the reverse of what one would expect based on the stoichiometry of VSe$_2$.

Fig. 4.15 provides more detail on the vanadium-enriched chunks found in the aged suspension. Fig. 4.15(a) shows a generally rectangular chunk several microns in size imaged in both bright and annular dark-field scanning mode. It is evident that the chunk has considerable variation in thickness. The thickness variations are also highlighted in Fig. 4.15(b), which shows a bright-field TEM image of a detail from the chunk shown in Fig. 4.15(a). Fig. 4.15(c) shows STEM images of a different chunk, much larger than that shown in Fig. 4.15(a-b), again with annular dark-field STEM inset. Thickness variations can also be seen in this chunk, although it is clearly thicker than any of the surrounding flakes. Alongside the generally square shape, this makes it unlikely that the chunks formed directly from VSe$_2$. Instead, it seems likely that they precipitated out of solution in the same way as the selenium nanowires did. Fig. 4.15(b) shows a HR-TEM image of part of a chunk, with its FFT inset. Unfortunately, it is was not possible to identify consistent lattice fringes in direct space, the FFT reveals that the material has both polycrystalline and amorphous components.

Based on these observations, it is likely that when kept in propylene carbonate for relatively little time, VSe$_2$ nanoflakes decompose into their elemental constituents.
Figure 4.14: TEM analysis of nanowires and porous chunks that form in two-day-old VSe$_2$ suspension in PC. (a) Low-magnification image showing VSe$_2$ flakes, Se nanowires, and vanadium-enriched chunks. (b) HR-TEM image of Se nanowire with a lattice spacing of 0.45 nm. (c) FFT of nanowire shown in (b), demonstrating rectangular symmetry. (d) Dark-field STEM image indicating region of nanowire selected for EDS analysis (red box). (e) EDS map of nanowire vanadium signal. (f) EDS map of nanowire selenium signal. (g) Dark-field STEM image indicating region of porous chunk selected for analysis (red box). (h) EDS map of chunk vanadium signal. (i) EDS map of chunk selenium signal.
Figure 4.15: Additional images of chunks that formed in 2-day-old VSe\(_2\) PC suspension. (a) Bright-field STEM image of a large chunk resting atop an ultrathin VSe\(_2\) flake, with dark-field STEM image inset. (b) Zoomed-in bright-field TEM image of chunk featured in (a). (c) bright-field STEM image of a very large chunk connected to the copper grid and surrounded by several large VSe\(_2\) ultrathin flakes, with dark-field STEM image inset. (d) high-resolution TEM image of part of a chunk, with FFT inset.

4.4. Conclusions

From these experiments, we have determined that Scotch\textsuperscript{®} tape provides the thinnest mechanically-exfoliated flakes, followed by low-residue blue poly tape, and that Kapton\textsuperscript{®} tape is wholly unsuitable for VSe\(_2\) exfoliation. Furthermore, an annealing temperature of 350°C is acceptable in a vacuum oven for removing adhesive residue, so long as samples are not exposed to air for too long. However, the mechanical exfoliation process for VSe\(_2\) is difficult and has a steep learning curve\textsuperscript{52}. The thinnest samples I was able to achieve in the lab were at least 5 nm and had neither acceptable density nor uniformity. Therefore, I chose to explore the suitability of a newer method: electrochemical

\textsuperscript{52}It seems like the ideal number of hands for maintaining tension on the two tapes while pulling them apart while also keeping the angle between the two tapes small is > 2.
It proved to be facile to exfoliate large quantities of ultrathin VSe$_2$ flakes following the procedure outlined by Yu et al.\textsuperscript{154}. The resultant flakes were characterized using atomic-resolution TEM down to 20 K, AFM, AFM, and Raman spectroscopy to detail the oxidation and degradation process, MFM to explore changes in the ferromagnetic response over time, and TR-MFM as a proof of concept for the technique. We were also able to clarify process parameters that affect the quality of electrochemically exfoliated VSe$_2$ ultrathin flakes: any delay in removing the solvent, including delays in drying time, from the VSe$_2$ contributes to significant degradation of monolayer and bilayer regions of the flakes. This degradation initially manifests as a lacelike network of holes, and eventually as the decomposition of the VSe$_2$ into selenium nanowires and a porous sponge consisting primarily of vanadium. Damage can be mitigated by performing the exfoliation and drop-casting process quickly—ideally less than 45 min total for exfoliation, drop casting, and transfer to vacuum chamber—and minimizing the drying time. Fortunately, both propylene carbonate and oxidation damage were also shown to only locally affect the surface fields measured by MFM rather than leading to widespread quenching of the ferromagnetism. However, changing to an electrolyte solvent with a higher vapor pressure and lower reactivity may be a more fruitful avenue for reliably producing high-quality ultrathin VSe$_2$ flakes. It was also shown that FDT passivation can occur in dilute ethanol solution and that the passivation efficacy depends on concentration. Additionally, the previously reported method of a simple acetone rinse proved insufficient for removing excess FDT\textsuperscript{154}. In addition to the obvious step of rinsing with a clean-drying solvent such as isopropanol or methanol after acetone, a rapid thermal annealing cycle proved necessary to collect meaningful TEM data without massive carbon contamination. Device applications will likely require similar processing for clean electrical contact. Finally, VSe$_2$ was demonstrated to be a viable candidate for rapid top-down electron beam nanosculpting, which will enable highly-customizable dry nanopatterning for advanced devices.
CHAPTER 5 : Conclusions and Future Work

5.1. Bismuth Selenide Conclusions and Future Work

5.1.1. Nanosculpting

The Bi$_2$Se$_3$ nanosculpting project sought to address the material effects of thinning and carving Bi$_2$Se$_3$ with a Ga$^+$ focused ion beam and the feasibility, facility, and utility of instead using a TEM beam to both thin and carve Bi$_2$Se$_3$. These top-down resist-free dry patterning processes could be used for the creation of complex device geometries necessary for applications such as topological quantum computing. We found that ablating Bi$_2$Se$_3$ with a FIB led to local depletion of selenium atoms, an expansion of the lattice constant, and the formation of an edge band adjacent to the material that was composed of a mixture of crystalline and amorphous phases and that the crystalline phases did not appear to match patterns associated with Bi$_2$Se$_3$. We were also able to establish that aside from the formation of these edge bands, there did not appear to be any cracking or fracturing of the material, which addressed an outstanding question in the literature: why Aharonov-Bohm measurements of FIB-cut nanowires indicated a lower wire diameter than was measured topographically using AFM$^{54,60}$. Experiments with TEM cutting of Bi$_2$Se$_3$ yielded much cleaner results in terms of debris, but they also provided a few caveats. The process of TEM sculpting Bi$_2$Se$_3$ structures was facile, but with thicker samples it could also become extremely time-consuming. In addition, it was found that the physical orientation of the sample inside the TEM column was absolutely vital to successful nanosculpting. If the sample did not face away from the TEM beam with the window atop it, ablated material would redeposit randomly at the carving site and form extremely robust structures capable of outlasting 100 nm of SiN$_x$ under direct 200 keV electron irradiation without any visible sign of distress$^{65}$. The identity of these robust crystals was not determined, but some FFTs suggested that they may have a body-centered cubic or tetragonal structure.

There are multiple directions this project could lead in the future. One of the most important for understanding the processes would be to perform cross-sectional TEM on both FIB-and TEM-thinned samples of Bi$_2$Se$_3$ so that a depth profile for the damage caused by each beam can be established and so that ac-STEM can establish both defect types caused by the beam and the degree
of gallium doping that FIB-thinned samples undergo. Atomic-resolution EDS may also be able to identify at least the stoichiometry of the material formed by face-up TEM sculpting, and potentially other methods of material identification such as XPS may be tried. Nanosculpting in either the F200 or the NEOARM at the University of Pennsylvania would likely lead to a substantial improvement in beam accuracy and therefore successful device production, as the stage drift that complicated the process in the 2010F will not be present. While unfortunately the face-down requirement for in situ TEM sculpting of Bi$_2$Se$_3$ precludes the ability to perform simultaneous transport measurement, production and then measurement of TEM-sculpted devices is also a logical next step. Finally, it may also be worthwhile to pursue an annealing study of FIB-sculpted and TEM-sculpted Bi$_2$Se$_3$ nanostructures to determine if the lattice constant can be restored and if the selenium deficiency can be corrected via controlled heating in a selenium-rich environment.

5.1.2. Alloying

After the fortuitous discovery that metallic palladium is absorbed by Bi$_2$Se$_3$ at temperatures far below the melting point of either and produces a superconducting compound, my work served to further our understanding of what happened during the reaction at the nanoscale$^{15}$. Through TEM, EDS, and Raman measurements, we were able to determine how annealing temperature affected the spread of Pd through Bi$_2$Se$_3$ flakes and whether the palladium appeared to replace either of the components of Bi$_2$Se$_3$. The nanostructure of the palladium-alloyed regions is overwhelmingly polycrystalline, likely as a result of the speed and magnitude of the reaction, which is extensive. While the identity of the superconducting compound remains a mystery, we were able to determine some information about the results of the reaction. The reaction does not appear to impact the ratio of bismuth to selenium to a major extent in the alloyed regions, so the reaction does not appear to be any sort of substitution. Both thinner flakes and flakes annealed to higher temperatures both exhibit more palladium spread, but in all cases the Pd seems to incorporate itself in a relatively uniform front. Additionally, the reaction products were shown to be stable over the span of several months, which is necessary for broad-scale implementation.

I also investigated whether other metals would behave similarly to palladium when annealed in the presence of Bi$_2$Se$_3$. I determined that neither niobium nor tungsten would react up to 450°C, at which point the Bi$_2$Se$_3$ decomposed into a variety of micron-scale crystals, some of which were determined to be body-centered cubic in structure. On the other hand, both iron and nickel were
found to react fairly extensively with Bi$_2$Se$_3$ upon annealing, which is promising because devices combining magnetic and topologically insulating materials may demonstrate interesting or useful transport phenomena.

Iron, unfortunately, was found to rust extremely rapidly after the annealing process, which precluded it from further study, but nickel did not encounter this setback. While nickel is in the same group as palladium, it was shown to react in a very different manner: whereas palladium propagated along a uniform front within the material and formed a very abrupt interface with normal Bi$_2$Se$_3$, nickel both clearly traveled along edges and lattice vectors within the flakes, causing noticeable bulges and cracks, and suffused them. All Bi$_2$Se$_3$ flakes annealed in the presence of nickel exhibited a small background signal throughout their bulk that outlined them against the silicon nitride window. Additionally, while with palladium the deposited metal was often found to be completely absorbed by the Bi$_2$Se$_3$ flakes, none of the nickel wires were found to be completely consumed. While this reaction was more pervasive than the localized but massive absorption of palladium, and while it appeared to cause some visible distortion to the lattice, it did not have a similarly deleterious effect on the Bi$_2$Se$_3$ crystal structure. Overwhelmingly, Bi$_2$Se$_3$ flakes annealed with nickel retained their characteristic diffraction patterns, but the diffraction patterns themselves often started to exhibit additional features. Many of the features observed in the diffraction patterns resemble those presented by Koski et al.\textsuperscript{99} in their report on chemical intercalation of zero-valent metals, so it is possible that an intercalation reaction is also occurring in this system. However, some results in the EDS suggest that in high-nickel areas, there is also a depletion of bismuth and an enhancement of selenium, so the formation of nickel selenides cannot be ruled out as an additional reaction.

There remains plenty of further research that could be performed on alloying Bi$_2$Se$_3$ with nickel and palladium that would help both determine the nature of these reactions and investigate their use. As the reaction products of both the nickel and palladium systems remain unkown, cross-sectional TEM, atomic-scale EDS, and XRD or XPS could all help determine the final composition and depth distribution of reactants. In addition, for both systems extremely low-temperature annealing could help control the reaction process, and in the case of Pd:Bi$_2$Se$_3$, could also potentially assist in producing larger crystals suitable for analysis. In the case of Ni:Bi$_2$Se$_3$, MFM measurements may help determine whether or not the annealing products are magnetically responsive, although scanning SQUID measurements would also be highly suitable. Transport measurements of Ni:Bi$_2$Se$_3$ would
also be informative, especially at low temperature. If a meaningfully-sized crystal of the superconducting phase produced in the Pd:Bi$_2$Se$_3$ system can be obtained, further transport characterization of it is also called for. Given the high level of disorder found in the palladium-alloyed regions, it is probable that parameters such as the transition temperature and critical field are incorrect, and likely below their true values.

5.2. Vanadium Selenide Conclusions and Future Work

My final research in the Drndić lab focused on developing research capability for further study of the in-plane 2D ferromagnet vanadium selenide. Through my research we were able to rule out micromechanical exfoliation as a high-yield method of obtaining monolayer VSe$_2$ in the lab and fine-tune the process for electrochemical exfoliation instead. In addition, we performed a thorough materials investigation, defect, degradation, and oxidation study of VSe$_2$ prepared via electrochemical exfoliation and passivated with different concentrations of a chemical reported in the literature to be effective$^{154}$. We found an extremely strong dependence of material quality on the speed at which the nanoflakes could be removed from the exfoliating solution, determined at least one product of the decomposition reaction that takes place in VSe$_2$ in propylene carbonate$^{53}$, found that even heavily-damaged regions of few-to-monolayer VSe$_2$ remained ferromagnetic, and determined that the passivation efficacy of FDT was concentration-dependent and that even concentrations as low as 5 mM provided substantive protection from oxidation. We were also able to determine that propylene carbonate is a moderately effective solvent of PMMA and confirm my hypothesis that the acetone-only cleaning method presented by Yu et al.$^{154}$ was altogether insufficient for removing excess carbon residue. Instead, a subsequent rinse in isopropanol and a rapid thermal annealing cycle proved effective. Finally, I also determined that TEM nanosculpting of VSe$_2$ is extremely facile, which opens the door to in situ TEM transport and sculpting experiments.

These results were only the beginning of my planned VSe$_2$ project, so much remains to be done. Transport measurement of VSe$_2$ remains a priority, as well as the aforementioned in situ sculpting and transport measurement. Lorentz TEM was attempted with VSe$_2$ but has so far been unsuccessful, and developing the capability to directly image VSe$_2$ magnetic fields at resolutions superior to MFM would be desirable. The PPC transfer procedure outlined in Section 2.1.3 has been established for thicker samples of mechanically-exfoliated VSe$_2$, but it needs to be extened to the

$^{53}$Indeed, this is a facile, if roundabout, method of producing selenium nanowires.
passivated ultrathin flakes produced by electrochemical exfoliation and also modified to incorporate hBN stamping for both encapsulation and the production of magnetic tunnel junctions. Once this has been accomplished, production and measurement of twisted bilayer VSe$_2$ should commence, as well as the fabrication and testing of the device concept that initiated this project: VSe$_2$/Bi$_2$Se$_3$ SOT-MRAM. Stretch goals for my project also included the development of a lab recipe for CVD growth of VSe$_2$ and VS$_2$, as well as work into the creation of VSSe Janus nanosheets.

5.3. Contributions to Facilities

During my research at the University of Pennsylvania, in addition to performing research on novel materials with high-value applications, I oversaw an expansion of both the Drndić lab’s and the Singh Center for Nanotechnology’s capabilities for 2D material preparation and analysis. In the Singh Center, I arranged for the installation of a 505 nm laser and ultranarrow notch filter in the confocal Raman instrument, developed institutional knowledge about Lorentz TEM, and prepared a standard operating procedure for the Gatan ULTDT liquid helium TEM holder that the Drndić lab acquired for low-temperature in situ transport and Lorentz measurements inside the TEM. Within the Drndić lab, I spearheaded the return to cyrogenic transport and materials analysis as well as an entirely new project focused on 2D ferromagnetic materials. In service to this, I:

- Successfully funded my Bi$_2$Se$_3$ research with an NSF Graduate Research Fellowship
- Originated the idea for the VSe$_2$ project and successfully co-wrote an NSF EAGER grant to fund it
- Managed the acquisition, installation, repair, and training for the closed-cycle LHe probe station and its peripherals
- Managed the acquisition, installation, and training for a new Bruker MultiMode® 8-HR AFM
- Invented an entirely new method of AFM to investigate lateral surface magnetic fields of VSe$_2$
- Designed new lithography masks and developed optical lithography recipes for producing in situ transport TEM chips
- Designed and built electronics for transport measurement within and outside a TEM including breakout boxes and signal filters
• Oversaw the refurbishment of the argon glove box for handling air-sensitive samples

• Designed TEM chip carriers and parts for the 2D material transfer stage

• Wrote instrument control software for the Keithley 6221/2182a stack, the AMI 430 magnet power supply, the LakeShore 336 Temperature Controller, and the Keithley 2400 SourceMeter

• Designed and built a small electrochemical exfoliation station for preparation of VSe$_2$

In addition, as a result of my work into 2D materials specifically for electronics and spintronics, the Drndić lab has also decided to acquire a Janis closed-cycle $^3$He refrigerator with a rotating sample holder to allow for measurement of transport under the effects of both in-plane and out-of-plane magnetic fields.
Figure A.1: (a) Single-chip design for 20-lead wafer pattern. (b) Dose test lithography pattern with dose factors for the test listed on the sides (outer, inner).

Figure A.2: (a) Wafer-scale design for the 12-lead 3 mm × 4 mm chips with SiN$_x$ windows. (b) Single-die design for 12-lead window chips.
Figure A.3: (a) Wafer-scale design for the 16-lead 2.4 mm × 3.8 mm chips with SiN$_x$ windows. Note the quality of life feature on the pads mask of arrows on the edges directing the user to the location of the alignment marks. Since the pads are patterned first, these features will be visible during back-side alignment for the TEM windows. (b) Single-die design for the 16-lead window chips. (c) Central detail of the 16-lead window chips, showing additional alignment marks.
Figure B.1: TEM sample stage for 2 mm × 4 mm SiN$_x$ window chips that I designed and was made in the David Rittenhouse Labs machine shop from lead-free brass.
Figure B.2: Sample clip for 2 mm \times 4 \text{ mm} TEM stage that I designed and which was made from spring bronze by the David Rittenhouse Labs machine shop.
Figure B.3: Brass holder I designed along with Jerome Mlack (who 3d printed the original part) for the micromanipulator for the transfer stage so that it could be securely mounted on a lab jack.
Figure B.4: Brass platform I designed along with Jerome Mlack (who 3d printed the original part) for the sample arm in the microscope transfer stage. Threaded 1/4" bolt holes are provided for the transfer arm itself to be mounted securely in place, but we typically used a large binder clip instead, as it allowed for more freedom to reposition the arm as necessary.
Figure B.5: Diagram of the cuvette holder for electrochemical exfoliation. Measurements are in mm. Cuvette holder was 3D printed from ABS plastic with an infill of 50%. The outer cage of the holder is 25 mm wide and has square “legs” that are 6.25 mm wide. The total width of the cage is 25 mm. In the center of this structure, there is a square cutout with side length 13.5 mm that extends from the top of the structure down into the base. This cutout securely holds the cuvette and prevents it from sliding or tipping within the cage.
Figure B.6: Design of the breakout box that I drafted, machined, and built for the probe station and other transport measurement apparatuses. The left set of connections is for triaxial TNC cables, as are installed in the probe station, and the right set of connections is for biaxial BNC cables. Inputs and outputs are connected via double-pole double-throw (DPDT) switches that are set to on (connected), float (instrument grounded, DUT floating), and ground (instrument and DUT grounded). To avoid ground loops, the ground is set up as a star ground with a common copper strip. The TNC bulkheads are connected to banana jack binding posts to interface with the Keithley 6221/2182A stack, which use alligator clips and spades to connect. The TNC bulkheads are also connected to a second set of DPDT switches so that the sheaths may also be grounded or connected to a guard voltage for shielding. Effort was made to ensure that all component terminals were made from either gold- or silver-plated copper to minimize thermoelectric EMFs and contact resistances; connecting wires were made of unplated copper; and Kester cryogenic solder (which had the smallest difference in work function compared to copper) was used to secure connections. Due to the high lead content of this solder, the breakout box is likely not ROHS-compliant.
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