

Observation of Novel Charge Ordering and Study of Unique Interlayer Oxidation in VdW Itinerant Ferromagnet Fe_3GeTe_2

A Thesis

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by

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Certificate

This is to certify that this dissertation entitled ‘Observation of Novel Charge Ordering and Study of Unique Interlayer Oxidation in VdW Itinerant Ferromagnet Fe_3GeTe_2 ’ towards the partial fulfillment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents study/work carried out by ‘Piyush Uttam Parakh at Indian Institute of Science Education and Research, Pune’ under the supervision of ‘Dr. Aparna Deshpande, Assistant Professor, Department of Physics’, during the academic year 2022-2023.



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This thesis is dedicated to my parents

Declaration

I hereby declare that the matter embodied in the report entitled ‘Observation of Novel Charge Ordering and Study of Unique Interlayer Oxidation in VdW Itinerant Ferromagnet Fe_3GeTe_2 ’ are the results of the work carried out by me at the Department of Physics, Indian Institute of Science Education and Research, Pune, under the supervision of Dr. Aparna Deshpande and the same has not been submitted elsewhere for any other degree



Piyush Parakh

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Abbreviations

0D	Zero D imensional
1D	One D imensional
2D	Two D imensional
3D	Three D imensional
AFM	A tomical F orce M icroscopy
CDW	C harge D ensity W aves
FFT	F ast F ourier T ransform
FGT	Fe ₃ GeTe ₂
FWHM	F ull W idth H alf M axima
HOPG	H ighly O riented P yrolytic G raphite
HR-TEM	H igh- R esolution T ransmission E lectron M icroscope
LDOS	L ocal D ensity o f S tates
LT-UHV-STM	L ow- T emperature U ltra- H igh- V acuum S TM
PC	P olycarbonate
PCB	P rinted C ircuit B oard
PDMS	P oly d imethylsiloxane
STM	S canning T unneling M icroscopy
STS	S canning T unneling S pectroscopy
TBG	T wisted B ilayer G raphene
TMDC	T ransition M etal D ichalcogenide
TSP	T itanium S ublimation P ump
VdW	V an d er W aals

Abstract

Low dimensional materials show unique properties as compared to their 3D counterparts which make them a fascinating system to study. The paradigm shift in the study of 2D materials happened when Andre Geim and Konstantin Novoselov isolated a single atomic layer of graphite known as graphene in 2004. The field of 2D materials is an active area of research that encompasses a wide range of materials such as metals, insulators, semiconductors, and superconductors. One such material is the vdW itinerant ferromagnet Fe_3GeTe_2 (FGT) with a Curie temperature of 220 K, which retains its ferromagnetic properties up to monolayer.

In the first part of the thesis, various vdW materials like graphite, NbSe_2 , MnPS_3 , hBN and Fe_3GeTe_2 have been studied using techniques such as AFM, Raman spectroscopy, HR-TEM and transport measurements. Successful isolation and characterization of monolayer graphene was achieved followed by the preparation of TBG (Twisted Bilayer Graphene) with a twist angle of 8.7° . Band gap of MnPS_3 was calculated to be 2.75 eV by studying its heterostructures with graphene. Exfoliation of FGT was performed with the thinnest flake obtained to be a trilayer. Intensity of Raman modes at 120 cm^{-1} and 154 cm^{-1} were found to be enhanced with decreasing thickness of the exfoliated FGT flakes. A few FGT crystals were found to have excess Fe concentration which are accommodated either in-between the layers or inside the layer.

FGT is known to be an air-sensitive material that oxidizes in ambient conditions. Oxidation was studied on exfoliated FGT flakes where surface oxidation starts at around 4 hours of exposure with rate of oxidation increasing exponentially with temperature. Raman modes are shifted to 124 cm^{-1} and 142 cm^{-1} for oxidized flakes hinting at structural change in the flakes. Thickness of the FGT flakes was found to increase in a sigmoidal fashion which is explained by oxygen intercalation in between the FGT layers. Interlayer oxidation in FGT is hypothesized considering the oxidation of the protected side exfoliated on PDMS and confirmed through transport measurements.

In the second part of the thesis UHV-STM at 4.2 K has been used to study the surface of FGT at the atomic scale. STM images revealed regions of FGT that were pristine and Fe-intercalated. Also various kinds of intrinsic atomic vacancies namely - Te, Fe I and Fe II defects were imaged and identified unambiguously. Charge ordering is observed in Fe-intercalated regions in FGT samples as $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulation as well as $2a_0 \times a_0$. Spectroscopy measurements showed a decrease in Kondo temperature for Fe-intercalated regions.

Keywords: 2D Magnetism, Charge Ordering, Fe-intercalated FGT, Surface and Interlayer Oxidation of FGT.

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Chapter 1

Introduction

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1.1 Overview

Ever since humans have acquired the ability to think, the workings of the physical world has aroused an unsatiating curiosity among their minds. Some of the great minds have taken on this journey to uncover the truths of the universe, leading to knowledge and methods of acquiring it, which is known as science in modern times. Specific understandings of the universe, such as matter, energy, force, and space-time, are grouped together and studied under the banner of Physics. Physics had its humble beginnings around 5000 years ago when ancient people used to gaze at stars and started calculating time using its motions. Since then, physics as a field of study has grown enormously, encompassing subjects such as condensed matter, astrophysics, high-energy physics, quantum mechanics, and relatively.

Among these, condensed matter physics is by far the most extensive field of study, which can proudly proclaim to have a third of all physicists working on it [1]. The field has reaped significant advancements in both theoretical and technological aspects, leading to the emergence of exotic phenomena such as superconductivity, Hall effect, and the much-celebrated invention of transistors. Condensed matter physics, in its most general sense, is the study of condensed phases of matter, especially solids and liquids. The scope of condensed matter physics employs a wide range of phenomena with length scales ranging from a few angstroms to meters and temperatures ranging from nano kelvins to thousands of kelvins.

The work done in the thesis is in the field of condensed matter physics, specifically focusing on nanoscales, cryogenic temperatures, and ultra-high vacuum.

1.2 From Isolated Atoms to Exotic Materials

1.2.1 The Formation of Matter

Atoms, the building block of literally everything in the universe, are made up of elementary particles called fermions, such as protons and neutrons that together form the nucleus and electrons that form the outer shell of the atom. When these atoms come close together, they experience a kind of interaction known as electromagnetic force, which is one of the four fundamental forces of nature, of which the other three are gravity, weak, and strong force. When many atoms come together, they form matter that condenses into various phases according to the strength of interaction between the atoms and are classified as solids, liquids, gases, plasma, and some exotic phases. These phases of matter are interchangeable and can be tuned by parameters such as temperature, doping, and pressure, which causes the material to undergo a phase transition. Figure 1.1 (a) displays a schematic diagram of the formation of solids beginning with isolated atoms.

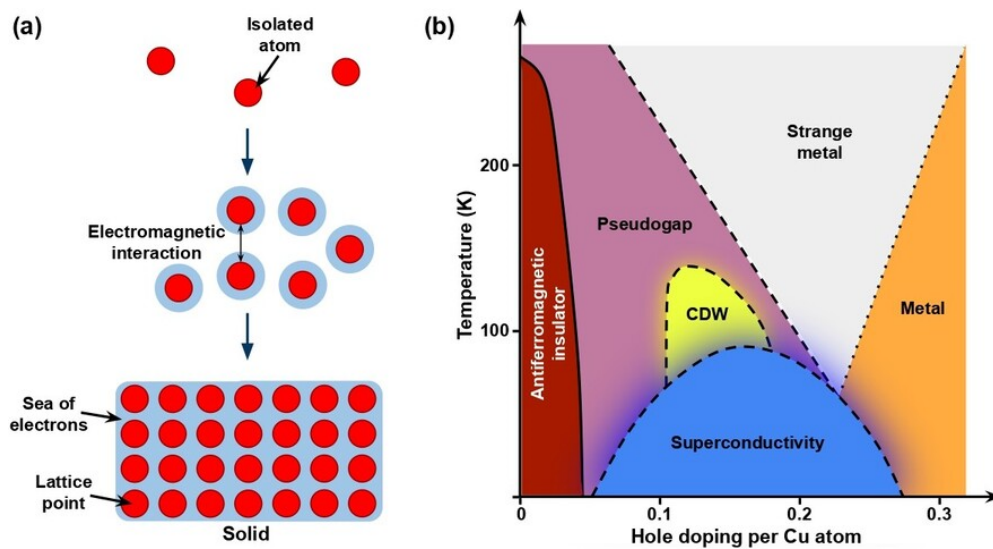


Figure 1.1 | Isolated Atoms to Exotic Materials. (a) Schematic representation of the formation of solids with top panel depicting isolated atoms and bottom panel showing the structure of solids. (b) Schematic phase diagram of cuprate superconductors.

The total energy of solids is lower than the energy of all the isolated atoms together, with the difference in energy being termed as binding energy and is given as

$$E_b = \frac{1}{N} (E_{tot} - NE_0)$$

where E_b is the binding energy, N is the number of atoms, E_{tot} is the total energy of the solid and E_0 is the energy of the individual isolated atom. The binding energy attains its lowest value at a particular distance between the atoms, where it forms a stable solid. Solids in which atoms are arranged in translational periodicity are called crystals, and the corresponding atomic arrangement is labeled as a lattice. The smallest portion of the crystal that can be repeated to get the entire structure is called a unit cell, which can be in hexagonal, square, or honeycomb shape, to name a few. The simplest theory to explain the properties of solids is the free electron model. According to the theory, electrons in solids can be classified into two types: one are valence electrons, which are bound to the atoms or lattice, and the other are free electrons called conduction electrons, which form a sea of particles around the lattice. The valence electrons play no role in the physics of solids and are considered inert, while the conduction electrons are the ones that drive most of the physics of solids.

1.2.2 Electronic Correlations and Exchange Interactions

Electrons play a major role in the physical and chemical properties of solids. Various theories are put forward to explain the behavior of solids, taking into account the interactions between electrons, with the simplest being the Fermi gas, where all the electrons (fermions) are thought to be non-interacting. Introducing interactions between these fermions gives rise to fermi liquid theory, which is used to explain many real systems such as metals, semiconductors, and insulators. Further increasing the interactions leads to fermions that are strongly correlated and can be seen in materials such as Mott insulators and heavy fermionic systems.

There are many elementary excitations in solids, such as excitons, which are electron-hole pairs, and phonons, which are quanta of lattice vibrations. Electrons may also interact with these excitations and cause exotic phenomena to emerge, such as superconductivity and CDW, and are grouped under electronic correlations. The interaction between like particles is known as exchange interaction and is responsible for the magnetic properties in the system. Exchange interaction and electronic correlations are competing phenomena which is readily seen in superconductivity-magnetism competition and CDW-magnetism competition. [Figure 1.1 \(b\)](#) shows the phase diagram of a typical cuprate superconductor where different phases,

such as CDW, superconductivity, and magnetism, can be seen to compete with each other and are separated by solid and dashed lines that mark the phase boundary.

This thesis has attempted to study fundamental properties such as charge density waves using crystals as a medium.

1.3 Magnetism, Charge Density Waves and Superconductivity

1.3.1 Magnetism

One of the earliest fundamental properties to have acquired the attention of mankind is magnetism, and its study started around 2500 years ago. Magnetism is generally a low-temperature phenomenon where thermal fluctuations are not strong enough to destroy magnetism [2]. Magnetism in a material arises through two factors (i) the spin of quantum mechanical particles and (ii) the motion of charged particles called orbital moment. The magnetic properties observed are generally through a coupled interaction of spin and orbital moment. These magnetic moments interact with each other through exchange interaction and give rise to long-range magnetic order thus giving magnetic properties to materials.

Materials can be classified based on the type of magnetic behavior they exhibit such as paramagnetic, diamagnetic, ferromagnetic and antiferromagnetic. Materials that have no inherent magnetization but develop magnetism when placed in an external magnetic field are paramagnetic, diamagnetic materials are materials that oppose the external magnetic field. Materials that exhibit magnetic order in the absence of an external magnetic field in which spins are aligned parallel to each other are ferromagnetic and the antiparallel alignment leads to antiferromagnetism.

1.3.2 Charge Density Waves

Peierls' in 1930 introduced the concept of CDW [3]. He predicted that a linear chain of atoms with uniform electronic density would become unstable at sufficiently low temperatures [4]. This leads to a modulation in the charge density of electrons known as charge density waves. The redistribution of electron density simultaneously causes a lattice modulation and the system breaks translational periodicity. Figure 1.2 (a) shows a 1D chain of atoms with uniform lattice spacing 'a' and the corresponding band structure is shown on top. As the temperature is lowered, the Fermi surface becomes unstable and the system undergoes a CDW transition leading to lattice modulation as shown in Figure 1.2 (b). The corresponding

band structure is shown on top with a gap opening at the fermi level which lowers the total energy of the system.

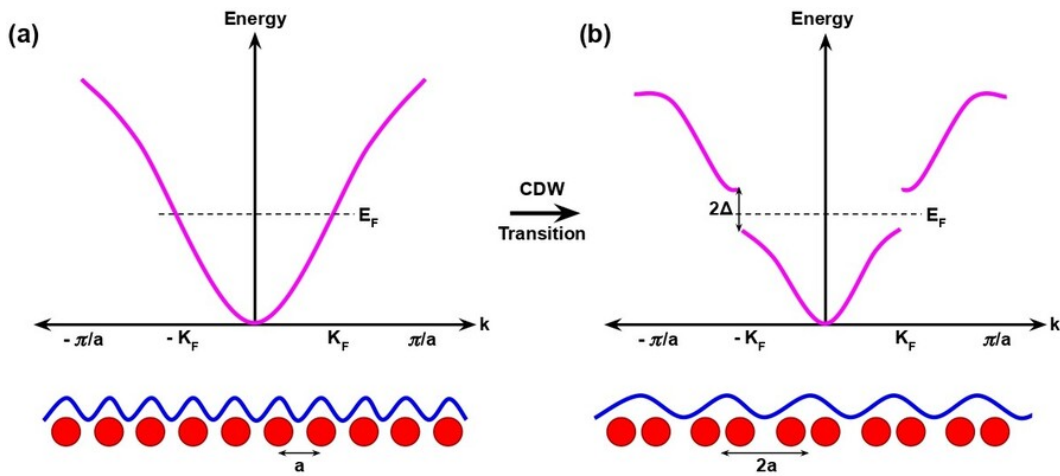


Figure 1.2 | Peierls' Instability. (a) The lattice is shown in red with a blue curve representing periodic charge density and the corresponding electronic band structure on top. (b) Modulated charge density along with reconstructed lattice and its corresponding band structure on top showing a gap of 2Δ around the Fermi level.

Since the inception of CDWs in 1D systems, CDWs have been found in 2D, 3D and quasi 2D materials. The most extensively studied class of materials is van der Waals (vdW) transition metal dichalcogenides. Various mechanisms have been put forward to explain the origin of CDW in these systems like Fermi surface nesting in which a single wave vector can span the whole Fermi surface, Kohn anomaly and electron-phonon coupling [5]. To date, no universal mechanism explaining CDW has been put forward with every new CDW discovered that leads to new phenomena. Further, CDWs in a material can be tuned by external factors such as strain, pressure or intercalation [6].

1.3.3 Superconductivity

One of the hottest topics of research in the scientific community ever since its discovery by Kamerlingh Onnes in 1911 is superconductivity [7]. It is the property of a material having zero electrical resistance and is always accompanied by an expulsion of magnetic field which is known as the Meissner effect. Superconductivity can be brought about in a material by either lowering its temperature, increasing pressure, or by doping it. The temperature below which a material transforms into a superconductor is known as transition temperature and the magnetic field above which a superconductor becomes a normal material is called the critical

magnetic field. The most widely accepted theory to explain superconducting phenomena is the BCS theory proposed by Bardeen, Cooper and Schrieffer in 1957 [8]. BCS theory states that when a material is in a superconducting state, the electrons have a net attractive interaction and form cooper pairs. This interaction is mediated through phonons and all the cooper pairs in a superconductor are correlated.

In 1986, a new class of superconductors was discovered that had a transition temperature of 35.1 K and increased up to 133 K in ambient conditions in the material which is a cuprate of mercury, barium and calcium [9]. Standard BCS theory is unable to explain the phenomena related to these materials and thus these materials came to be known as unconventional superconductors while the ones explained by superconductivity are known as conventional. Their transition temperature being higher than the conventional ones gives them the title of high-temperature superconductors. High-temperature superconductivity has been observed in many classes of materials with the recent ones being iron-based superconductors in 2006 [10]. To date, there has been no universal theory to explain the phenomena of superconductors in all materials, and is an active area of research.

1.4 Outline of Thesis

The thesis is written in a way so as to incorporate an overview of the methods followed for various types of experiments which will be helpful for students and researchers new in the field. I have tried my best to keep the language as simple as possible and get technical wherever necessary.

The thesis is divided into two sections considering the two types of work done namely ‘**Surface and interlayer oxidation induced changes in vdW ferromagnet Fe_3GeTe_2** ’ and ‘**Atomic scale fingerprints of excess Fe in Fe_3GeTe_2** ’. The first half of the thesis covers Chapters 3 to 6 and the second half covers chapters 7 to 9.

Chapter 2 gives brief information about the class of materials used in the work with the spotlight being on FGT. **Chapter 3** starts with methods of exfoliation, identification, and characterization of flakes followed by methods of forming micro-electrical contacts. Different types of transfer techniques to make heterostructures are discussed. **Chapter 4** presents the work done on various vdW materials with a main focus on graphite and MnPS_3 . Twisted Bilayer Graphene is characterized by AFM and Raman spectroscopy, followed by the determination of the MnPS_3 band gap by studying the transport properties of their

heterostructures. **Chapter 5** starts with the study of general properties of FGT such as exfoliation and phonon modes followed by characterizing different types of Fe-intercalation in FGT. **Chapter 6** focuses on the oxidation properties of FGT such as surface oxidation and interlayer oxidation. Oxidation properties are studied in both ambient conditions and heating using techniques such as Raman spectroscopy, AFM, and transport measurements. **Chapter 7** gives basic information on the theory and operating principle of STM and STS. Different components and working of the LT-STM instrument used for the study are mentioned. Methods of STM tip preparation and sample preparation are discussed. **Chapter 8** starts with the study of pristine FGT followed by a detailed study of various types of defects. Observation of Moiré pattern is also mentioned. **Chapter 9** starts with $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ reconstruction in Fe-intercalated FGT followed by an in-depth study of different types of charge ordering and their interplay with each other and pristine structure. **Chapter 10** gives an overall summary of the results obtained, their interpretation, further studies, and new prospects that the study has opened.

All the crystal structures were made using VESTA software and all schematic diagrams were made using Google Slides. OriginPro was used for plotting graphs. AFM and STM images were processed using SPIP software.

Chapter 2

Materials of Study

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2.1 2D Materials

2.1.1 Materials at Low Dimensions

Most of the experiences of the common man with the physical world are with objects that are perceivable to its naked senses. These objects are classified as 3 dimensional (3D) considering the three different coordinates used to specify their size. When the dimensions of one of the axes are within a few nanometers limit, it is referred to as two-dimensional (2D) material e.g. graphene. When dimensions in any two of the axes are restricted to a few nanometers, it is referred to as one-dimensional (1D) material, e.g. carbon nanotubes and when all three dimensions are in nanometers limit, it is referred to as zero-dimensional (0D), e.g. quantum dots. [Figure 2.1](#) (a) shows a schematic representation of materials in the 3D, 2D, 1D, and 0D limits from left to right.

Materials at lower dimensions show unique optical, chemical, and mechanical properties than their 3D counterparts [11] which makes them a fascinating subject to explore. Due to their reduced dimensions, they are an ideal source for many technological applications especially in the chip industry.

2.1.2 VdW Materials

A class of materials that exhibits interesting properties due to their unique structure and reduced dimensions are vdW materials. They are layered materials that have strong intralayer bonding and weak interlayer vdW bonding which gives them characteristics that are in between 2D and 3D range and are thus also referred to as quasi-2D materials. The weaker

vdW forces between the layers make it possible to cleave the layers which leads to thinning down of the material and eventually obtaining two-dimensional (2D) flakes that are a few nanometers thick to even atomically thin samples as shown in [Figure 2.1 \(b\)](#). The ways of achieving this can be broadly classified into two methods: a top-down approach like exfoliation or a bottom-up approach like chemical vapor deposition.

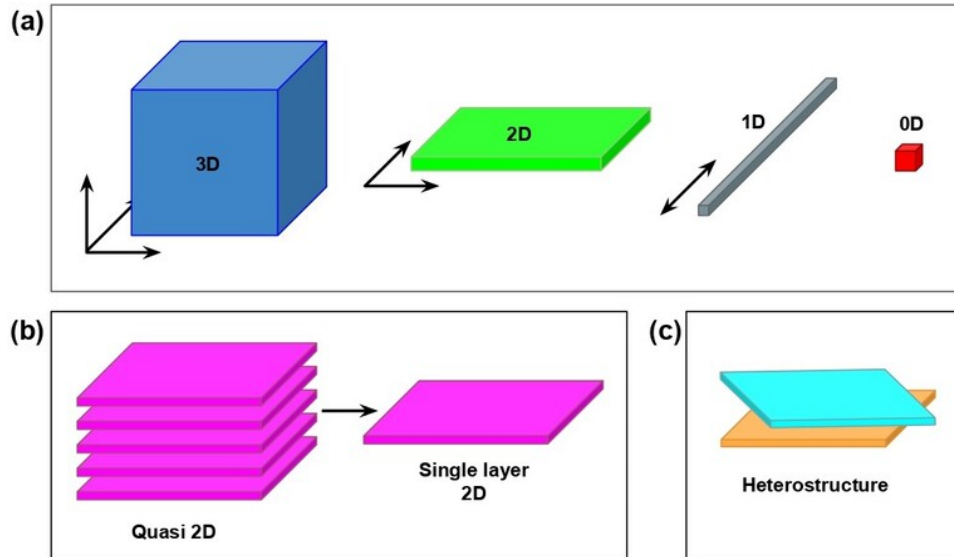


Figure 2.1 | Materials at Low Dimensions. (a) Schematic diagram of materials at different dimensions starting from 3D followed by 2D, 1D, and 0D from left to right. (b) Schematic diagram of quasi two-dimensional material on the left with the right side showing its isolated single layer. (c) Schematic representation of a heterostructure made of two different 2D materials.

2D materials have novel properties than their 3D counterparts, such as high carrier mobility, good thermal conductivity, and increased surface-to-volume ratio. These interesting properties of 2D materials make them a promising candidate for constructing various electronic, valleytronic, and optoelectronic nanodevices [12]. Also, their physical and chemical properties can be tuned by methods such as strain, gating, proximity effects, and moiré patterns with ease [13].

2.1.3 Tailoring of VdW Materials

Since 2D materials do not require lattice matching, layers of different materials can be stacked on top of each other resulting in properties that can be wildly different from their initial counterparts. Such structures are known as heterostructures. A schematic diagram of a typical heterostructure is shown in [Figure 2.1 \(c\)](#). Layers of the same materials can be stacked

on top of each other with a twist angle between them which gives rise to moiré patterns and the resulting structure being known as homostructure.

The vdW gap between the layers can accommodate various types of ions and atoms that can potentially change the dynamics of the parent material. The atom that is intercalated is called guest and the parent layer is called host, the interplay between guest and host can change the properties of the parent compound. The most sought-after elements to intercalate are Mn, Fe, Co, Ni, and Cu due to their potential applications in battery technology [14]. Depending on the nature of the intercalant atom, the fundamental properties of the materials can be altered such as magnetism, thermoelectricity, and electromagnetic wave absorption [15].

2.1.4 2D Magnetism

All these benefits of vdW materials have piqued the interest of researchers all around the world leading to extensive studies being conducted in the search for new vdW materials. The efforts have reaped their benefits with vdW materials now encompassing a wide range of materials including metals, semimetals, topological insulators, superconductors, and magnetic materials [16].

An area that has been of particular interest is 2D magnetism which has the potential to be used in the design of functional devices such as magnetic sensors and magneto-optical devices. Magnetic vdW materials have been around for some time but they do not retain their magnetic properties when exfoliated up to monolayer. The problem was triumphed over in 2017 when 2D magnetism was first observed in CrI_3 and $\text{Cr}_2\text{Ge}_2\text{Te}_6$ [17,18] compounds that are antiferromagnetic. Since then, many materials exhibiting magnetic behavior up to the monolayer limit have been synthesized such as antiferromagnetic MnPS_3 and ferromagnetic VSe_2 .

2.2 Fe_3GeTe_2

One of the newly emerging vdW materials that has the potential to be used in applications such as spintronics and to study fundamental physics such as 2D ising ferromagnetism is Fe_3GeTe_2 . FGT was first synthesized in 2006 along with Ni_3GeTe_2 by Kremer et al. [19] and since then it has become a sought-after material in the scientific community. FGT belongs to the family Fe_nGeTe_2 ($3 \leq n \leq 7$) where $\text{Fe}_{3,4,5}\text{GeTe}_2$ have been synthesized at the time of writing and theoretical calculations predict stable structures up to Fe_7GeTe_2 [20]. A summary of the properties of the FGT family is given in Table 2.1.

	PARAMET- ERS	Synthesize d	No. of Atomic layers	Monolayer thickness (nm)	Curie temperatu re (K)	Magnetic moment per Fe (μ_B)
MATERIAL						
Fe_3GeTe_2		Yes	5	0.82	220	2.87
Fe_4GeTe_2		Yes	6	0.97	266	2.73
Fe_5GeTe_2		Yes	7	1.09	332	3.18
Fe_6GeTe_2		No	8	1.10	450	2.94
Fe_7GeTe_2		No	9	1.12	570	2.91

Table 2.1 | Physical Properties of the FGT Family. The leftmost column depicts FGT with different stoichiometry and the topmost row depicts different parameters related to the materials.

FGT is a black metallic solid that crystallizes in a hexagonal system with space group $P6_3/mmc$ (No. 194) [19] and point group D_{6h} [21]. It oxidizes slowly in ambient conditions with reports on the rate of oxidations varying drastically from air-stable to oxidizing within a day [19,22]. It is an itinerant ferromagnet with a curie temperature of 220 K and shows strong perpendicular anisotropy with an easy axis being c that is stabilized due to spin-orbit coupling [23]. Experimentally observed values of Fe moment are in the range of 1.2 to 1.8 μ_B [24]. It has a room temperature conductivity of 2196.35 S/cm [25] which increases with decreasing temperature and rises again below 20 K [26]. It has two inequivalent Fe atoms based on its oxidation state with Fe (3+) labeled as Fe II and Fe (2+) labeled as Fe I.

Figure 2.2 (a) shows the side view of the crystal structure of FGT where the dotted rectangle shows the unit cell that contains 12 atoms in total. The lattice parameters are $a = b = 3.999 \text{ \AA}$ and $c = 16.33 \text{ \AA}$ with the angle between a and b being 120° . A single layer of FGT contains five atomic layers with the outermost layer consisting of Te atoms that crystallize in a hexagonal structure. Ge atoms are in the middle layer along with Fe II atoms both crystallizing in a hexagonal structure. The Ge-Fe layer is surrounded by Fe I atom layers on top and bottom which are also crystallized in hexagonal structure. The distance between interlayer Te-Te atoms is $0.375 \text{ \AA}$. Figure 2.2 (b) shows the top view of the crystal structure where the dotted polygon represents a unit cell. The hexagonal lattice of Te atoms can be observed clearly along with Ge and Fe I atoms. The Fe II atom sits directly under the Te

atoms. Figure 2.2 (c) shows the crystal structure of a single layer of FGT along with bonds between different atoms.

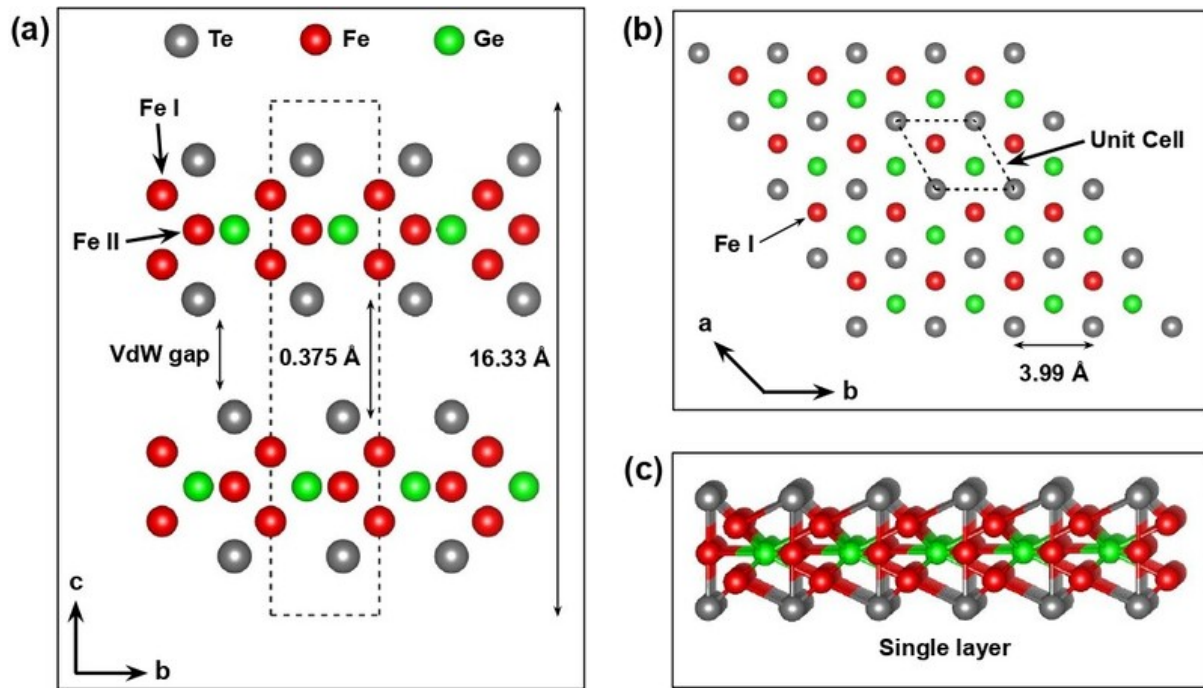


Figure 2.2 | Fe₃GeTe₂ Crystal Structure. (a) Side view of FGT crystal structure with dotted rectangle highlighting a unit cell. (b) Top view of FGT crystal structure. (c) A single layer of FGT showing its bonds.

The Monolayer of FGT was successfully exfoliated and shown to exhibit 2D using ferromagnetism with a transition temperature of 130 K [27]. Robust ferromagnetism with strong magnetocrystalline anisotropy was theoretically predicted [23] and confirmed by experiments in monolayer limit [28]. Magnetic properties can be tuned by strain [29] and also intercalation that achieved room temperature ferromagnetism in atomically thin flakes by ionic gating [30].

Heterostructures using FGT have been studied. Magnetoresistance has been extensively studied where a three-state MR state was proposed in FGT/graphene/FGT [31] and 160% magnetoresistance was observed in tunnel junctions of FGT/hBN/FGT [32]. Also, a homostructure of FGT with a twist angle of 87° was made that showed plateau-like magnetoresistance. Magnetisation of FGT can be controlled by a current known as spin-orbit torque which has been observed with 5 nm of heavy metal Pt sputtered on FGT [33].

Competition between ferromagnetism and anti-ferromagnetism is observed [34] with some reports suggesting an antiferromagnetic ground state for FGT [35]. Further, oxidation studies reveal antiferromagnetic coupling between oxidized and pristine parts [36].

Reports suggesting anti-ferromagnetic ground states along with strong electronic correlations coupled with its quasi 2D nature make it an ideal candidate to study various exotic phenomena like charge density waves and unconventional superconductivity. Further, the material having ferromagnetic properties up to monolayer makes it an ideal candidate for magnetic memory devices which are of great technological importance considering the large amount of data being generated [33,23].

All these parameters were taken into account before studying the material in detail with the primary motivation being its relatively high Curie temperature among all vdW materials.

2.3 Graphene and Beyond

2.3.1 Graphite

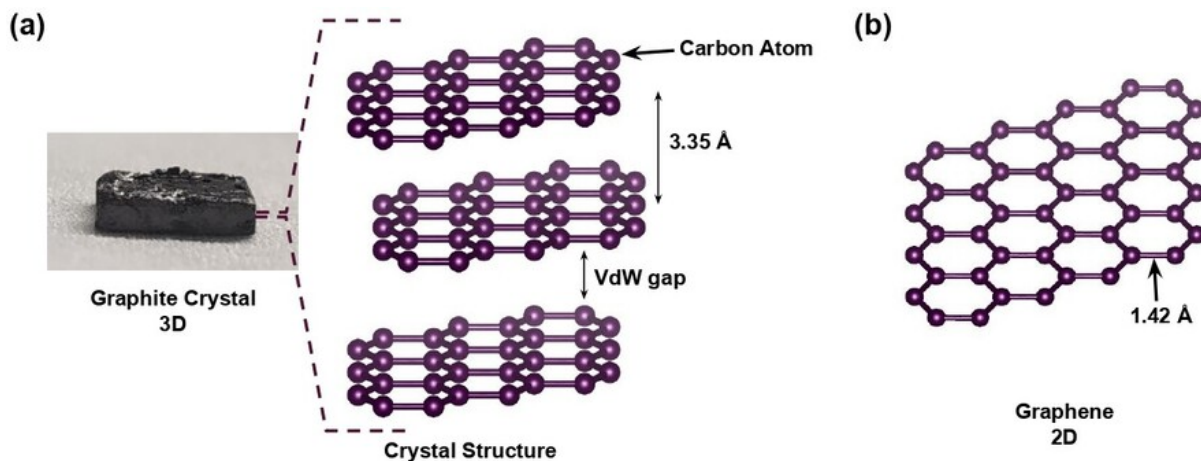


Figure 2.3 | VdW Material Graphite. (a) Graphite crystal on the left with the magnified image showing its crystal structure on its right. (b) A single layer of graphite known as graphene.

It all started with graphene when Andre Geim and Konstantin Novoselov successfully exfoliated graphite using scotch tape to obtain a single layer known as graphene [37]. This discovery won its researchers the Nobel Prize in 2010. Figure 2.3 (a) shows a highly ordered pyrolytic graphite crystal with the magnified part showing its crystal structure. It contains layers of carbon atoms crystallized in a hexagonal structure stacked on top of each other by vdW forces. Figure 2.3 (b) shows the crystal structure of a single layer of graphite known as

graphene. Graphene shows properties that are different from the bulk crystal such as zero band-gap, high flexibility, and high thermal and electrical conductivity earning it the title of ‘wonder material’ [16].

2.3.2 Other Materials

NbSe₂

NbSe₂ is a superconducting material with a transition temperature of 7.2 K in bulk and also shows CDW below 33 K in bulk. It comes under the family of transition metal dichalcogenides (TMDC). NbSe₂ can be used to induce superconductivity in other 2D materials through proximity effects [38].

MnPS₃

MnPS₃ is a wide gap semiconductor with a band gap of 2.64 eV and is antiferromagnetic in nature with a Néel temperature of 78 K and exhibits magnetic properties up to monolayer. It shows the property of spin-flop transition when a perpendicular magnetic field is applied [39].

hBN

hBN is a very good thermal and electrical insulator with a band gap of 5.9 eV. It is highly stable under environmental conditions which makes it an ideal material for the protection of environmentally degrading vdW samples [40].

Section I

Chapter 3

Experimental Techniques to Cleave, Stack and Probe VdW Materials

3.1 Exfoliation	16
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3.1 Exfoliation

3.1.1 Mechanical Exfoliation

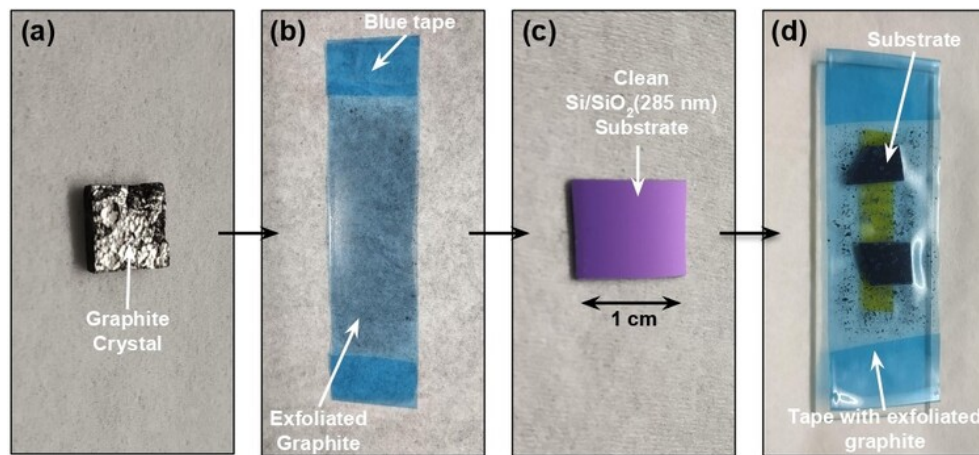


Figure 3.1 | Mechanical Exfoliation Process. (a) Graphite bulk crystal. (b) Illustration of graphite flakes exfoliated on cleanroom adhesive blue tape. (c) Clean and flat n-type Si/SiO₂(285 nm) substrate. (d) Transfer of flakes from the blue tape onto the substrate.

Mechanical exfoliation was done using cleanroom tapes such as scotch tape, green tape and blue tape. [Figure 3.1](#) shows the exfoliation process on highly ordered pyrolytic graphite (HOPG). An n-type Si/SiO₂ (285 nm) substrate of the desired size is cleaned by sonication in

acetone and isopropyl alcohol for 10 minutes and blow drying using nitrogen gas. The substrate was then oxygen plasma cleaned for 5 min at a power of 60 W. Si/SiO₂ (285 nm) substrate was used for exfoliation for all the experiments. A few layers of graphite crystals were first peeled on blue tape from the bulk crystal. The graphite crystals were exfoliated 8 to 12 times on the tape before transferring the tape onto the cleaned substrate. The tape is then removed slowly after 5-10 minutes leaving some of the exfoliated flakes on the substrate. Blue tape was used for all the exfoliation unless mentioned otherwise.

3.1.2 Liquid Phase Ultrasonication Exfoliation

Liquid phase ultrasonication exfoliation was done using acetone as the liquid medium. FGT crystals were immersed in acetone and sonicated for 1 hr to obtain nano-sized flakes suitable for Transmission Electron Microscopy (TEM) measurements. 2 to 3 drops of the solution were taken on a TEM grid and kept in vacuum conditions with 10⁻³ mbar pressure for 3 to 4 hours for drying. Acetone gets evaporated leaving behind nanosized exfoliated flakes on the TEM grid.

3.2 Identification and Characterization of Exfoliated Flakes

3.2.1 Optical Microscope

Optical contrast is defined as the difference between the reflectance from the substrate and from the flake. One of the ways to calculate contrast is given by,

$$C = \frac{I_{flake} - I_{subs}}{I_{flake} + I_{subs}}$$

where, C is the optical contrast, I_{flake} and I_{subs} are the intensity reflected from flake and substrate respectively. Silicon substrate with a SiO₂ thickness of 285 nm on top is used for all the experiments to visualize 2D materials due to the high optical contrast it generates [41]. White light was used for the illumination of all samples using an Olympus microscope. After exfoliation, the flakes of desired size and shape were identified using an Optical microscope and the thickness of the flakes is roughly determined using contrast generated by the substrate. Bulk flakes (more than 50 nm) reflect almost all light and as the thickness decreases, the flake becomes less opaque, and its contrast changes.

3.2.2 Atomic Force Microscopy

The thickness of the flakes was measured using AFM. Figure 3.2 (a) shows the AFM instrument where all the AFM data were acquired. AFM works on the principle of tip-sample interaction force as shown in Figure 3.2 (b). AFM is operated in three modes - (i) contact mode which works in attractive force region, (ii) non-contact mode which works in repulsive force regime and (iii) tapping mode which is in the intermediate of the two modes in which the tip vibrates near its resonance frequency. All AFM data were acquired in the tapping mode. Figure 3.2 (c) shows the schematic diagram of the working of AFM. The sample is placed directly below the tip which is connected to a piezoelectric scanner. The tip is then brought in contact with the sample using a controlled feedback loop. The piezoelectric scanner drives the tip in a raster motion on the selected area and the z height of the tip is recorded as an image according to the topography of the sample. The z height of the tip is controlled by the laser that is coupled to a feedback loop. The laser deflects according to the deflection in the tip which is caused by the changing topography of the sample.

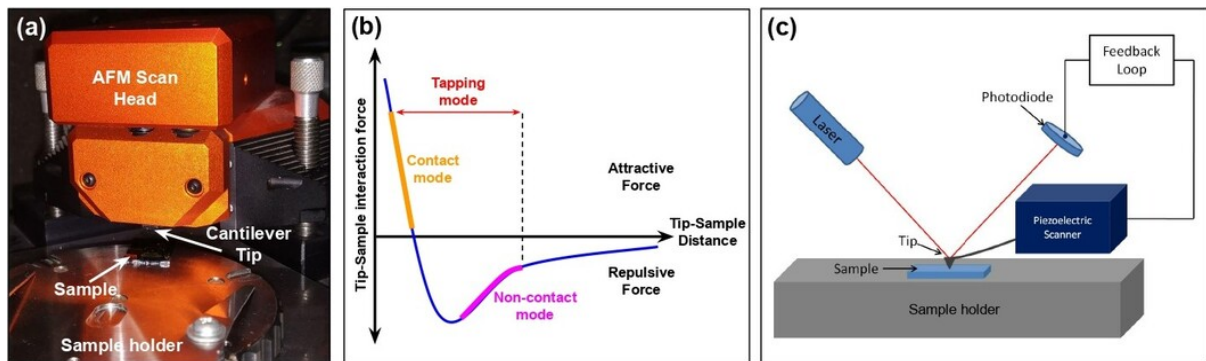


Figure 3.2 | Atomic Force Microscopy. (a) Nanosurf EasyScan 2 AFM instrument. (b) Schematic diagram of the working principle of AFM. (c) Schematic diagram of the operating principle of AFM.

3.2.3 Raman Spectroscopy

Raman spectroscopy is based on the phenomena of inelastic scattering of photons due to its interaction with phonons. It is widely used to characterize 2D materials due to their unique Raman peaks [42] and is also helpful in identifying the number of layers of certain vdW materials. Raman spectroscopic data were collected using a 532 nm excitation laser with a beam spot of 2 μm and laser power of 50 mW. The acquisition time and number of accumulations for graphene were 2 sec and 20 times respectively. For FGT acquisition time and number of acquisitions were 40 sec and 6 times. Raman data were collected using 50x

and 100x objective lenses for graphite and FGT respectively. All Raman measurements were performed in ambient conditions.

3.3 Micro-Electrical Contacts

3.3.1 Photolithography

Figure 3.3 (a) shows a Hall geometry pattern designed using CleWin software. Si/SiO₂ (285 nm) substrate was coated with positive photoresist using a spin coater operating at 4000 rpm for 1 min and then heated at 100 °C for 1 min. The photoresist-coated substrate was then exposed to laser light according to the desired pattern with a frequency of 405 nm with an energy density of 1300 mJcm⁻¹. The exposed part of the photoresist is degraded owing to its property of being light sensitive [43]. A developer solution is used to dissolve the degraded part and the desired pattern is developed as shown in Figure 3.3 (b).

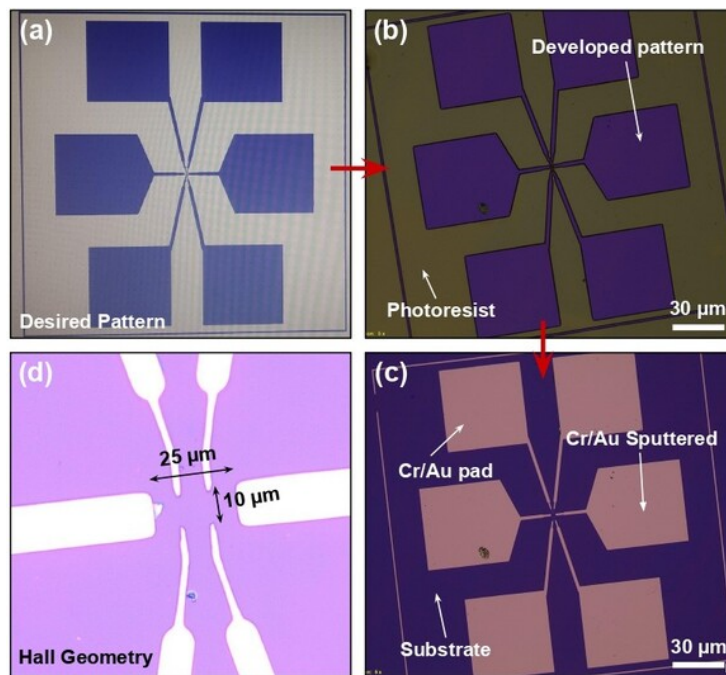


Figure 3.3 | Fabrication of Micro-Electrical Contacts. (a) Design of Hall geometry pattern. (b) Developed pattern after photolithography. (c) Pattern after sputter deposition of Cr/Au thin film. (d) Final Hall geometry micro-electrical contact.

3.3.2 Sputter Deposition

Sputtering deposition is a process in which high-energy ions are bombarded onto a target material causing its vaporization which is then deposited on the substrate forming a thin film.

The developed pattern was coated with a thin film of chromium (Cr)/platinum (Pt) acting as an adhesive followed by gold (Au). RF sputtering was done at a base pressure of 10^{-6} mbar and deposition pressure of 10^{-2} mbar in Argon atmosphere. The substrate was then kept in acetone for 1 to 2 hours removing the photoresist and leaving behind microcontacts as shown in Figure 3.3 (c). The photolithography process was optimized to get the best possible pattern. The hall geometry pattern is shown in Figure 3.3 (d)

3.3.3 Wire bonding

The substrate was then affixed to a Printed circuit board (PCB) using epoxy. The large Au pads were wire bonded to PCB using a gold wire of 25 μm thickness. The assembly was kept at 90 $^{\circ}\text{C}$ during the whole process.

3.4 Transfer Techniques

3.4.1 PDMS Dry Transfer Method

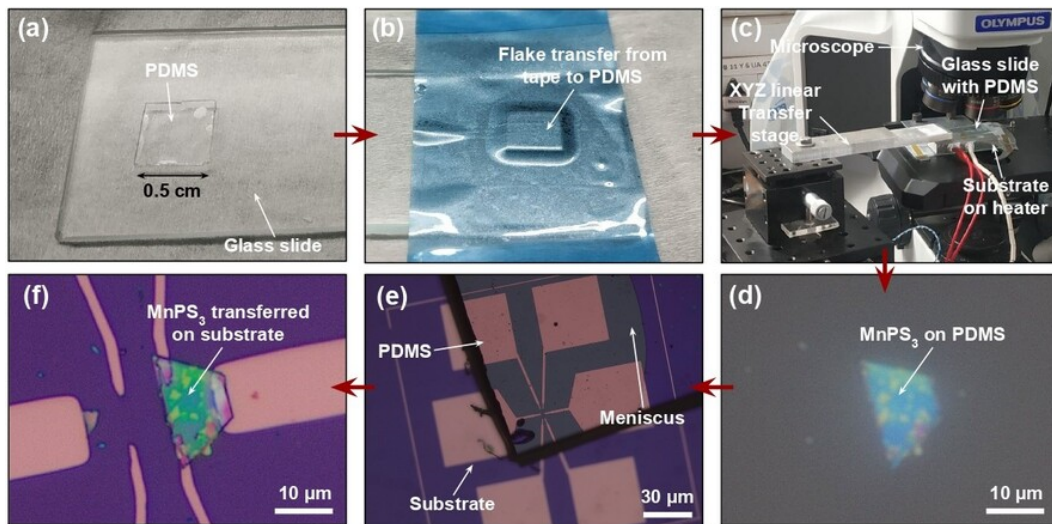


Figure 3.4 | PDMS Dry Transfer Method. (a) PDMS stamp on a clean glass slide. (b) Transfer of exfoliated flakes from cleanroom blue tape onto a PDMS stamp. (c) Transfer assembly with home-built transfer stage and microscope. (d) Optical microscope image of MnPS_3 flake on PDMS. (e) PDMS with the desired flake in contact with the target substrate. (f) MnPS_3 flake is deterministically transferred from PDMS to the target substrate.

Polydimethylsiloxane (PDMS) is a viscoelastic material used for lifting and transferring flakes [44]. A small piece of PDMS is applied on a clean glass slide as shown in Figure 3.4 (a). Exfoliated flakes on a cleanroom tape are transferred onto PDMS as shown in Figure 3.4

(b). The tape is then removed fast so as to get maximum yield. The glass slide is fixed onto a transfer stage assembly as shown in Figure 3.4 (c). Figure 3.4 (d-f) shows the process of transfer of a MnPS_3 flake. The PDMS is brought in contact with the target substrate slowly to avoid air bubbles. The contact can be seen as a meniscus is formed between the substrate and PDMS. The substrate is heated up to 90 °C for 5-10 min and the PDMS is lifted slowly for deterministic transfer.

3.4.2 Polycarbonate (PC) Film Dry Transfer Method

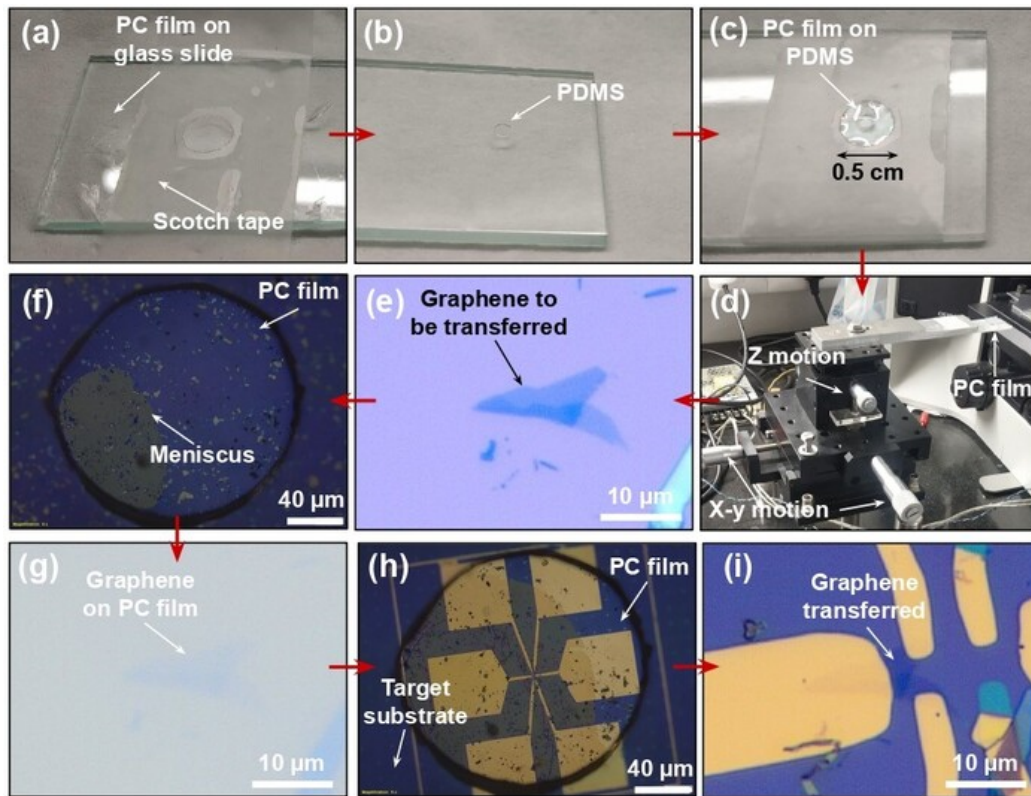


Figure 3.5 | PC Film Dry Transfer Method. (a) PC film on a clean glass slide. (b) Circular PDMS stamp on another glass slide. (c) PC film transfer set-up. (d) Transfer assembly. (e) Optical microscope image of graphene flake to be transferred. (f) PC film in contact with Substrate containing graphene. (g) Graphene lift-up on PC film. (h) PC film with graphene in contact with the target substrate. (i) Graphene flake is deterministically transferred from the initial substrate to the target substrate.

PC film is a high puncture resistance material having elasticity over a wide range of temperatures making it suitable for lifting and transferring flakes [45]. Figure 3.5 (a-c) shows the assembly of PC film. 6% w/w Poly(Bisphenol A carbonate) in chloroform is taken on a glass slide to form a PC film. The film is then lifted using scotch tape with a hole in between and transferred on round PDMS to form the desired system. Figure 3.5 (d-h) shows the

transfer process on a graphene flake. PC film is brought in contact with the substrate slowly with the desired flake, heated up to 60 °C for 5-10 min, and then cooled. The film is then lifted slowly to get the desired flake onto the film. The film is then brought in contact with the target substrate and heated up to 120 °C which melts the film along with the flake on the substrate. The substrate is then washed in chloroform to remove the film and the flake is deterministically transferred.

3.5 Transport Measurements

Transport measurements were taken in ambient conditions and dark environments on a probe station using a 2636 B source meter and 20 μm tungsten tips as probes for all measurements. The transport of FGT was taken by a home-built setup discussed in [Appendix A](#).

Chapter 4

Exploring Flatland Materials

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4.3 MnPS ₃ Band Gap Determination Through Heterostructures	28

4.1 Exfoliation of VdW Materials

	RESULTS	Total flake density	Thin flake density	Lateral size of flakes	Glue transferred
PARAMETERS					
More adhesive tape		More	Less	More	More
Heating the substrate		More	Less	More	More
Longer substrate-tape contact		More	More	More	-
More pressure while transferring		More	More	-	-
More crystal used		More	More	-	Less
More exfoliation on tape		More	More	Less	Less
Slow tape removal from substrate		More	More	More	-
Clean and flat substrate		More	More	More	-
Plasma cleaning		More	More	More	-

Table 4.1 | Exfoliation Parameters for Graphite. The leftmost column depicts different parameters of the exfoliation process and the topmost row depicts the results of the exfoliation process. (-) indicates no relation.

Scotch tape, green tape and blue tape were used for exfoliation. Scotch tape has the most glue of the three which results in strong adhesion and blue tape has the lowest adhesion with green tape in the intermediate. An optical microscope image of exfoliated graphite is shown in

Figure 4.1 (a). Bulk graphite flakes are yellow in color and the contrast changes from light blue to dark blue as the thickness decreases, finally reaching almost transparent as we go to the single nanometer limit. Exfoliation quality depends on many factors such as the adhesion of tape, the amount of crystal used, and the quality of the substrate. The exfoliation process was optimized using graphite and the results are summarised in **Table 4.1**. It was found that the best possible parameters to exfoliate are using less adhesive tape, heating the substrate while transferring, using more crystals for exfoliation, plasma cleaning the substrate before transferring, and having longer tape-substrate contact. Exfoliated graphite flakes will be referred to as graphene throughout the thesis with monolayer being specified as ‘monolayer graphene’.

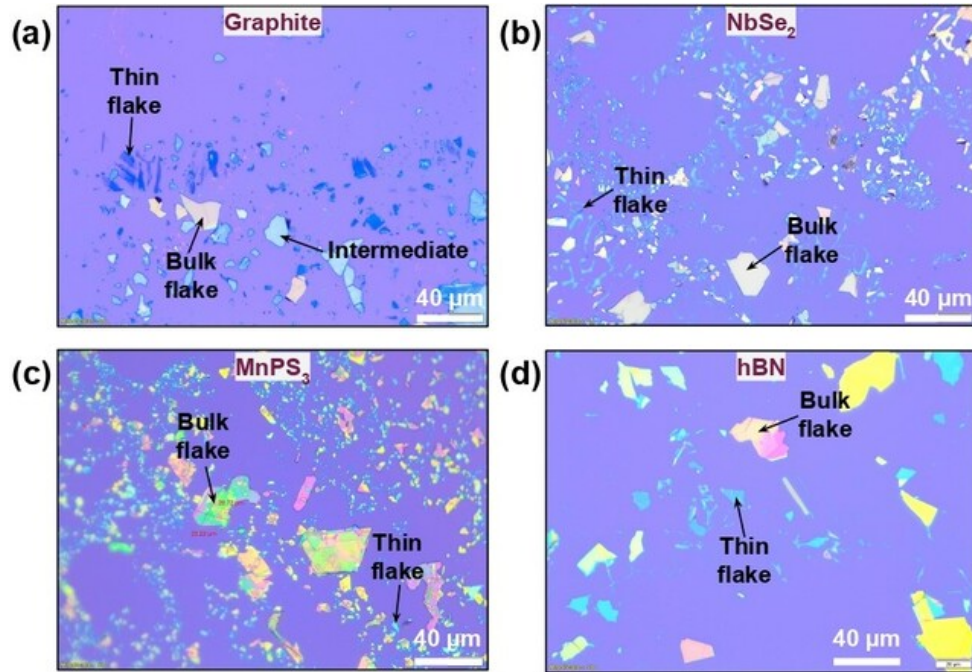


Figure 4.1 | Exfoliation of VdW Materials. (a) Optical microscope image of graphite exfoliation. (b) Optical microscope image of NbSe₂ exfoliation. (c) Optical microscope image of MnPS₃ exfoliation. (d) Optical microscope image of hBN exfoliation.

These parameters were also used for exfoliating NbSe₂, MnPS₃, and hBN, and the corresponding optical microscope images are shown in **Figure 4.1** (b), **Figure 4.1** (c), and **Figure 4.1** (d) respectively. MnPS₃ and hBN are semiconductors and insulators respectively which results in different colors of flakes observed. As the thickness reaches a few nanometers (5-10 nm), all flakes have blue contrast.

4.2 Monolayer and Twisted Bilayer Graphene

4.2.1 Monolayer Graphene

Monolayer graphene flakes were obtained after optimizing the exfoliation process. An Optical Microscope image of one of the flakes is shown in Figure 4.2 (a). This image will help in identifying other monolayer graphene by using its contrast. The area of the flake was calculated to be $50 \mu\text{m}^2$. Figure 4.2 (b) shows an AFM image of the flake where the monolayer is highlighted in black polygon. The height profile of the monolayer is shown in Figure 4.2 (c) and the corresponding line scan is shown by the blue dotted line in Figure 4.2 (b). The height of the monolayer was found to be 0.8 nm which matches the reported values [46].

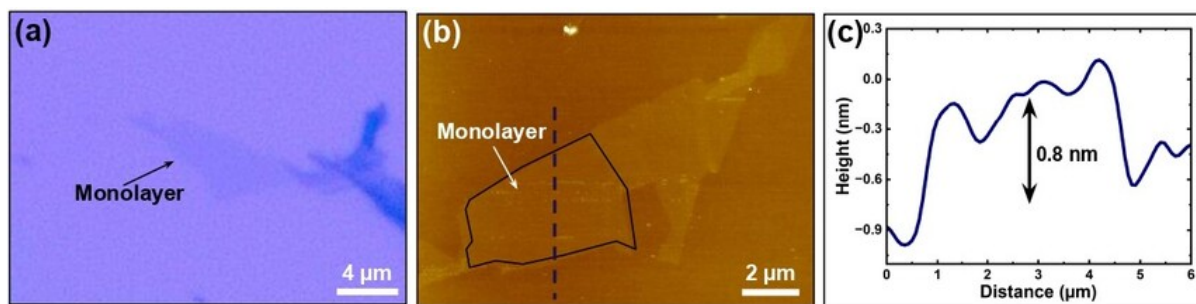


Figure 4.2 | Monolayer Graphene. (a) Optical microscope image of monolayer graphene. (b) AFM image of monolayer graphene highlighted in black polygon. (c) Height profile of graphene with the corresponding line scan marked by the blue dotted line in the image (b).

The flake obtained as a monolayer was confirmed by Raman spectroscopic measurements. Raman data of bulk flake, 4-5 layers, bilayer, and the monolayer were obtained and are shown in Figure 4.3 (b). Figure 4.3 (a) shows the corresponding optical images of the flakes where the marked region indicates the region of data acquisition. Graphite shows two main characteristic peaks, the G band at 1582 cm^{-1} and the 2D band at 2700 cm^{-1} [47]. The G band originates from normal first-order Raman scattering from the in-plane vibrational modes and the 2D band from the second-order in-plane vibrational mode. The G band's intensity peak is relatively larger than the 2D band for all the exfoliated flakes except the monolayer flake. The intensity of the G band is less than the 2D band for monolayer which is characteristic of graphene and confirms the obtained flake to be monolayer [48].

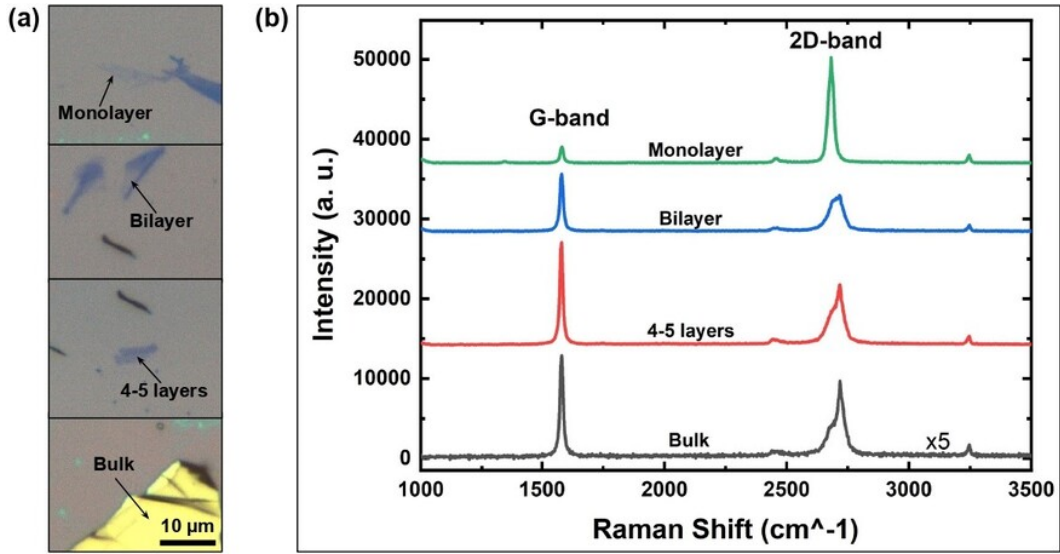


Figure 4.3 | Raman Spectroscopy of Monolayer Graphene. (a) Optical microscope images of monolayer, bilayer, 4-5 layers, and bulk exfoliated graphite flakes from top to bottom respectively. The scale bar is the same for all the images. (b) Corresponding Raman spectroscopic data acquired on the region marked in (a) where the bulk graphite is magnified 5 times.

4.2.2 Twisted Bilayer Graphene

When two monolayers are stacked on top of each other at a relative angle between them, it is known as twisted bilayer graphene. Twisted bilayer graphene (TBG) leads to the formation of moire patterns and has been extensively studied. TBG shows some interesting properties like superconductivity at a twist angle of 1.1° [49]. There are many ways to prepare twisted bilayer graphene like [50] PDMS transfer and using hBN as a tape.

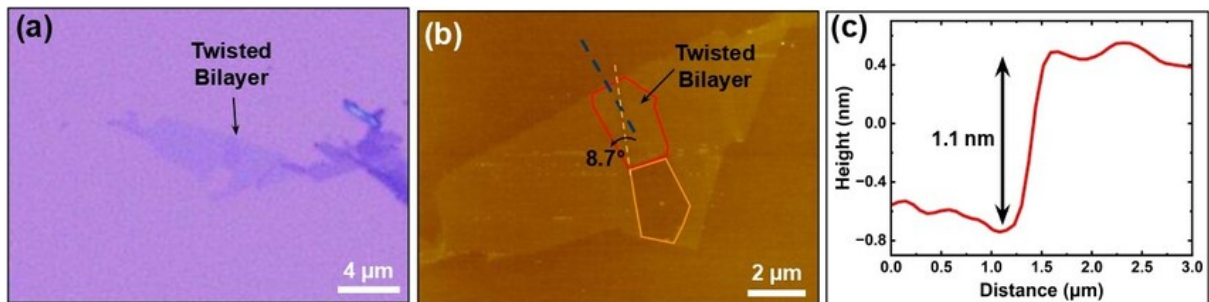


Figure 4.4 | Twisted Bilayer Graphene. (a) Optical microscope image of Twisted Bilayer Graphene. (b) AFM image of twisted bilayer graphene where the region highlighted in red polygon represents twisted bilayer and the yellow region shows the initial position of the lifted graphene. (c) Height profile of twisted bilayer graphene with the corresponding line scan marked by the blue dotted line in the image (b).A

Here AFM in contact mode was used for the reason that the tip gets into contact with the sample during scanning and can potentially alter the flake, especially thinner ones. An optical microscope image of the twisted bilayer is shown in Figure 4.4 (a). Figure 4.4 (b) shows an AFM image of the flake where the region marked by red polygon is the twisted bilayer. The region marked by orange polygon is the place from which the monolayer was picked and transferred. The twist angle was found to be 8.7° . The height profile of the TBG is shown in Figure 4.4 (c) with the corresponding line scan shown by the blue dotted line in Figure 4.4 (b). The calculated height of TBG is found to be 1.1 nm. The top view of the TBG crystal structure is shown in Figure 4.5 (a) where the graphene on top is depicted in orange and is rotated 8.7° with respect to the bottom graphene shown in red.

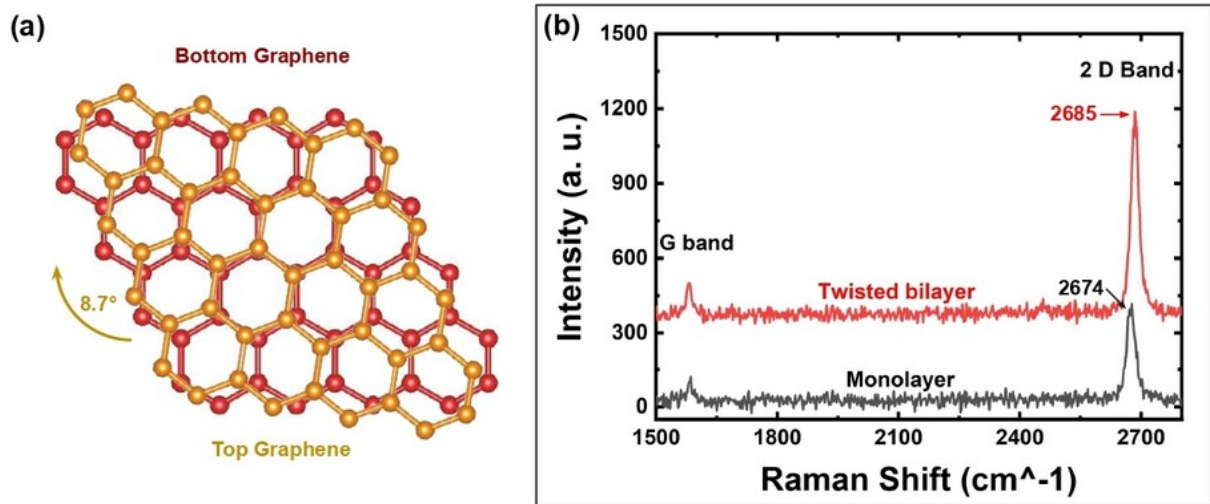


Figure 4.5 | Characterization of Twisted Bilayer Graphene. (a) Crystal Structure of TBG with top graphene (orange) is rotated at 8.7° to the bottom (red). (b) Raman Spectroscopy of TBG and initial monolayer.

Raman spectroscopy was conducted on both the monolayer and TBG separately and are shown in Figure 4.5 (b). The monolayer shows G band intensity to be lower than the 2D band as mentioned previously. TBG shows spectra similar to the monolayer where the G band has a lower intensity than the 2D band as opposed to the bilayer. There is a shift in the 2D peak which was found to be around 21 cm^{-1} . The full-width half maxima (FWHM) of the TBG was determined to be 21 cm^{-1} and that of the monolayer to be 12 cm^{-1} which is consistent with the reported data [51].

4.3 MnPS₃ Band Gap Determination Through Heterostructures

To calculate the band gap value of MnPS₃, heterostructures of MnPS₃ with graphene were made and studied with transport measurements under ambient conditions and dark environments except for photoluminescence measurements. Graphene will be referred to as ‘Gr’ in the heterostructures.

4.3.1 Gr-MnPS₃ Heterostructure

Gr-MnPS₃ heterostructure was prepared by first transferring MnPS₃ using the PDMS method shown in Figure 4.6 (a) on a pre-patterned hall geometry contact. Then, graphene was transferred on top of MnPS₃ using the PC film method shown in Figure 4.6 (b). The overlap region of graphene and MnPS₃ is shown in the 3D view of the AFM image in Figure 4.6 (c).

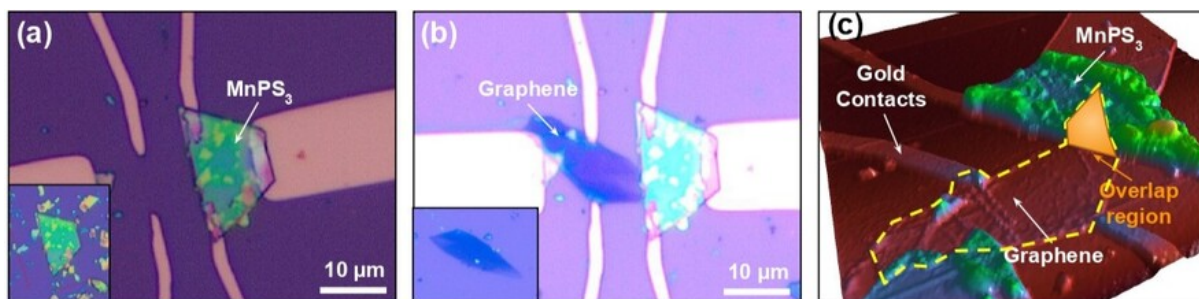


Figure 4.6 | Gr-MnPS₃ Heterostructure. (a) Optical microscope image of MnPS₃ flake transferred on pre-patterned Hall geometry contacts. The inset shows MnPS₃ flake before transfer. (b) Optical microscope image of graphene flake transferred on MnPS₃ flake and the contacts. The inset shows graphene flake before transfer. (c) A 3D view of AFM image of Gr-MnPS₃ heterostructure with orange shaded region highlighting the overlap of graphene and MnPS₃.

Transport measurements were taken on graphene and MnPS₃ separately to determine their characteristics. I-V characteristics of graphene are shown in Figure 4.7 (a). The thickness of the graphene was calculated using AFM giving an average of 5 nm with 1.2 nm at its thinnest part. Graphene shows linear behavior as expected, with resistivity calculated to be around $6 \times 10^{-6} \Omega\text{m}$ which is in line with the reported values of resistivity of graphene, which is of the order of $10^{-6} \Omega\text{m}$ for thickness less than 6 nm [52]. MnPS₃ shows semiconductor behavior evident from the photoresponse which shows an increase in current value as the flake is illuminated as shown in Figure 4.7 (b) and also from the I-V characteristics as shown in Figure 4.7 (c). Photoresponse was taken with a light of wavelength 465 nm at voltage = 1 V, with a time period of 10s. The shaded part shown in blue is the ‘light ON’ region. I-V

characteristics of Gr-MnPS₃ heterostructure are shown in Figure 4.7 (d). The positive probe is connected to MnPS₃, and the negative probe is connected to graphene. It shows Schottky-diode (metal-semiconductor) like characteristics. These measurements will be useful in testing if the future heterostructures prepared are of good quality.

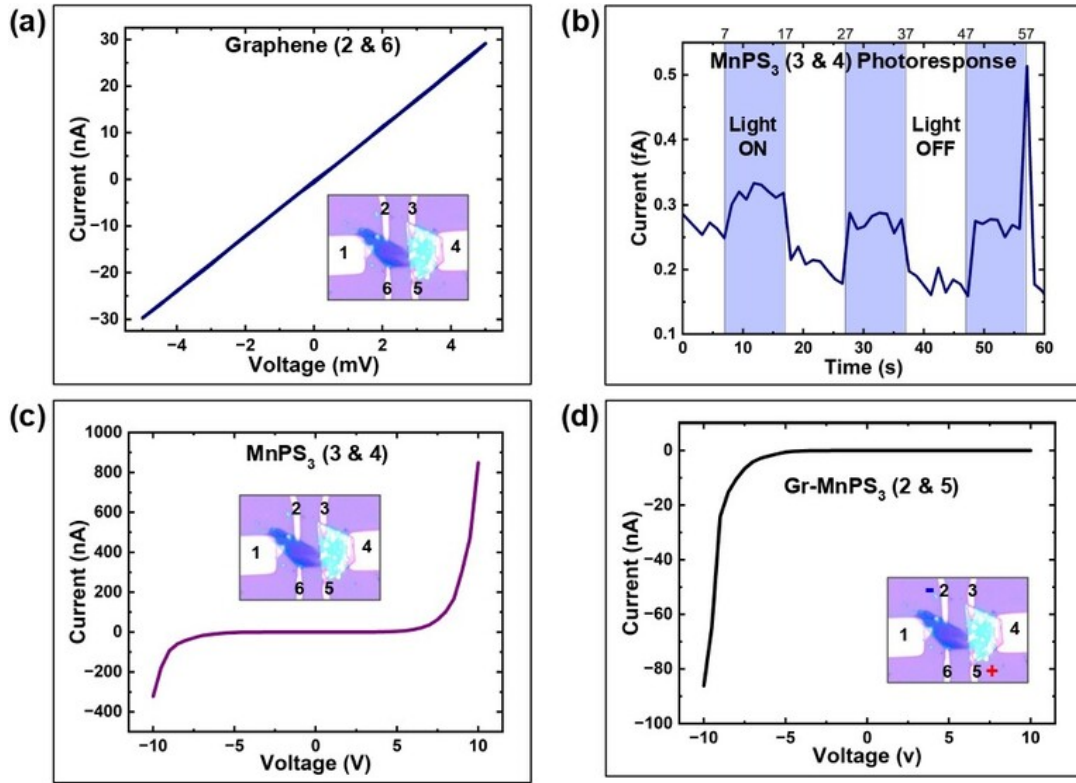


Figure 4.7 | Transport Properties of Gr-MnPS₃ Heterostructure. (a) I-V characteristics of graphene flake. (b) Photoresponse of MnPS₃ flake. (c) I-V characteristics of MnPS₃ flake (d) I-V characteristics of Gr-MnPS₃ heterostructure.

4.3.2 Gr-MnPS₃-Gr Heterostructure

Gr-MnPS₃-Gr sandwich-type heterostructures were prepared by the PDMS transfer method on pre-patterned contacts. The optical microscope images of the process are shown in Figure 4.8 (a-c) with the inset showing images of the respective flakes on PDMS before transferring. The MnPS₃ will act as a tunneling barrier between two graphite flakes. The overlap region is highlighted in orange as shown in Figure 4.8 (d) with an area of 200 μm². A 3D view of the AFM image is shown in Figure 4.8 (e) with a white dotted line representing the line scan shown in Figure 4.8 (f). The thickness of MnPS₃ was calculated to be 45 nm.

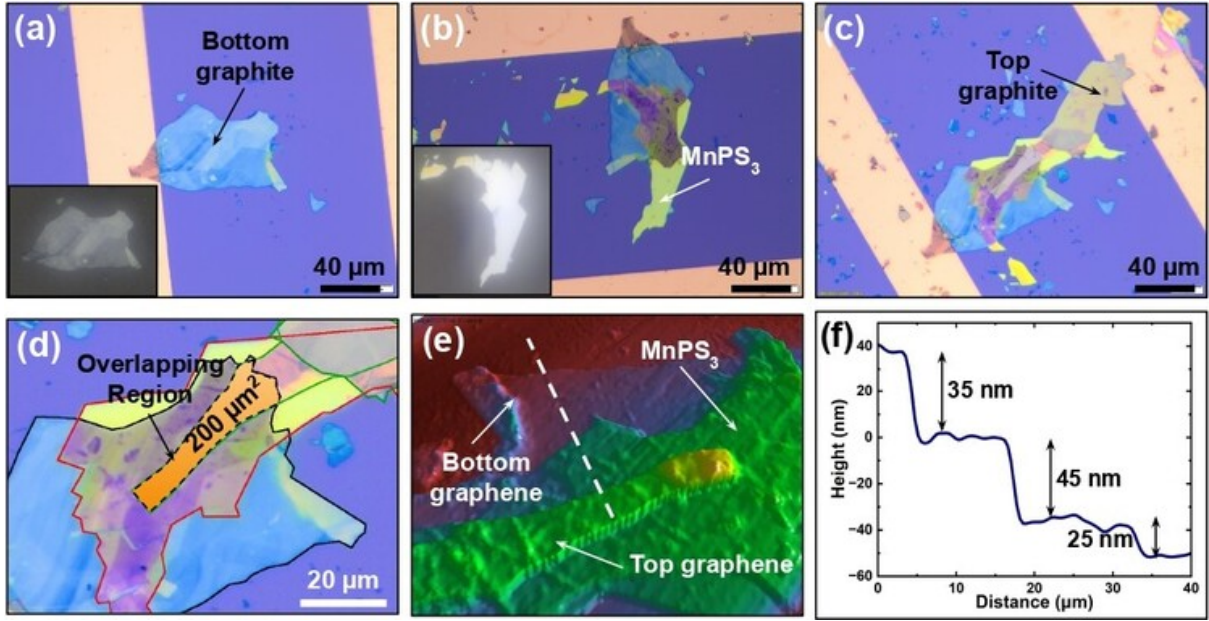


Figure 4.8 | Gr-MnPS₃-Gr Heterostructure. (a) Bottom graphene flake transferred on pre-patterned contacts. Inset showing the graphene flake on PDMS before transfer. (b) MnPS₃ flake transferred on graphene. Inset showing MnPS₃ flake on PDMS before transfer. (c) Top graphene flake transferred on MnPS₃. (d) The blue polygon highlights the bottom graphene flake, the red polygon highlights MnPS₃ flake, the Green polygon highlights top graphene and the orange shaded region shows the overlap of top graphene, MnPS₃ and bottom graphene. (e) A 3D view of the AFM image of the heterostructure. (f) Height profile of the heterostructure with the corresponding line scan shown by the white dotted line in the image (e).

The I-V characteristics and the corresponding $dI/dV - V$ graph of the heterostructure are shown in Figure 4.9 (a) and Figure 4.9 (b) respectively. The characteristics shown are similar to that of MnPS₃, which shows that there is no Gr-Gr contact between the layers and the tunneling junction produced is of good quality. The interlayer spacing in MnPS₃ is around 0.7 nm [53], so the tunneling junction of MnPS₃ is about 64 layers. The band gap of MnPS₃ is determined from the dI/dV curve by taking the slope at the point where the current changes drastically. The calculated band gap value is around 2.75 eV which is in excellent agreement with the reported data [54].

Figure 4.9 (c) Shows the band diagram of Gr-MnPS₃-Gr heterostructure with applied bias at room temperature. The contribution of current will come from both FN tunneling and direct tunneling till the bias reaches the band gap value and only FN tunneling after that. This gives an abrupt change in current when the potential difference applied is the same as the band gap. Thus, the band gap can be effectively calculated using the dI/dV plot.

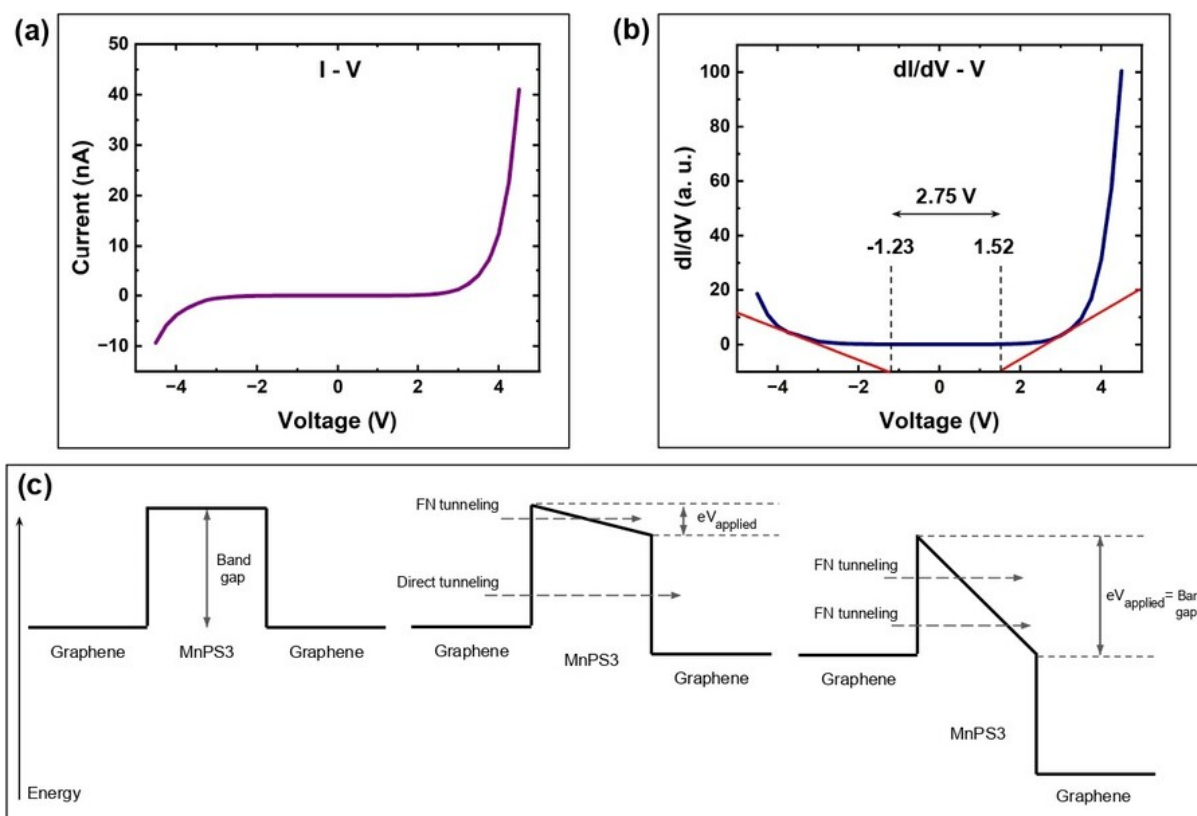


Figure 4.9 | Transport Properties of Gr-MnPS3-Gr Heterostructure. (a) I-V characteristics of the heterostructure. (b) Corresponding dI/dV -V characteristics showing band gap of MnPS₃. (c) Schematic diagram of the band diagram of the heterostructure without bias, with bias and bias equal to the band gap from left to right respectively.

Chapter 5

Characterization of Fe_3GeTe_2

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5.1 Exfoliation of FGT

FGT crystals were commercially purchased from 2D semiconductors. [Figure 5.1](#) (a) shows an optical microscope image of one of the crystals immediately after opening. It was found to be a black lustrous metal with a brittle texture. As FGT is an air-sensitive material [\[22\]](#), all experiments conducted with FGT were performed within one hour of exfoliation, and heating was avoided except for the experiments conducted in [Chapter 6](#).

Exfoliation of FGT was done using the optimized parameters except for the heating part to avoid degradation. Since the Te-Te vdW interaction in FGT is relatively stronger as compared to other vdW materials [\[55\]](#), it is a difficult material to exfoliate. One of the ways to get around this is to use more adhesive tape like scotch tape. Another method that was preferred throughout the experiments was to exfoliate the crystal swiftly by increasing the rate of peeling to separate the layers easily.

Exfoliation was done using blue tape and [Figure 5.1](#) (b) shows an optical microscope image of a typical exfoliation. It was found that the affinity of FGT flakes with the substrate is considerably more than other vdW materials studied resulting in more yield. Bulk flakes can be identified as yellow in color and reflect almost all light and thin flakes (less than 15 nm) have a dark blue contrast. The contrast changes from light purple to purple for the intermediate flakes with decreasing thickness. For very thin flakes (less than 7 nm), the contrast almost vanishes and the flakes are transparent. Thin flakes of around 10 nm

thickness were routinely obtained in all exfoliations. Figure 5.1 (c) shows the height profile of some of the flakes marked in Figure 5.1 (b).

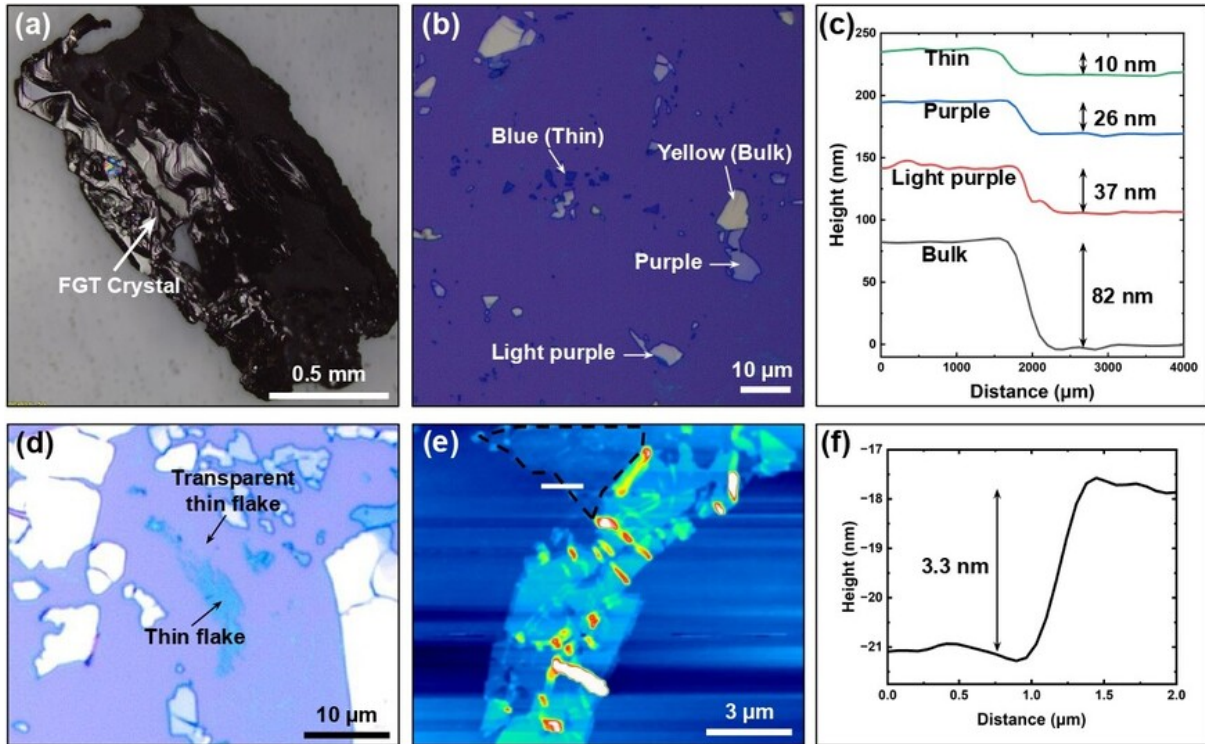


Figure 5.1 | Exfoliation of Fe_3GeTe_2 . (a) Optical microscope image of bulk FGT crystal. (b) Optical microscope image of a typical exfoliation of FGT marking flakes of various thicknesses. (c) Height profile showing correlation of thickness and contrast of the flakes in the image (b). (d) Optical microscope image of a thin FGT flake with the approximate location of the transparent flake marked. (e) The AFM image of the thin flake showing the transparent flake by a black dotted polygon. (f) Height profile of the transparent flake with corresponding line scan shown by the white line in the image (e).

Figure 5.1 (d) shows an exfoliated thin flake of 10 nm thickness with the approximate location of a transparent flake is marked. AFM image of the flake is shown in Figure 5.1 (e) where the transparent flake can be clearly identified and is marked by a black dotted polygon. Figure 5.1 (f) shows the height profile of the transparent flake with the corresponding line scan shown by the white line in Figure 5.1 (e). The height of the flake was calculated to be around 3.3 nm which gives the number of layers as three considering the height of a single layer to be around 0.82 nm [33].

5.2 Thickness Dependence of Raman Modes

Raman spectroscopy was performed to characterize the FGT flakes. Figure 5.2 (b) shows Raman data of bulk, thin, and intermediate flakes. Figure 5.2 (a) shows the crystal structure of FGT with pink and orange arrows representing approximate phonon vectors. A_{1g} Raman modes originate from out-of-plane lattice vibrations of Te and Fe I atoms and E_{2g} mode originates from in-plane lattice vibrations of all atoms with Te having phonon vectors in the opposite direction to that of Fe and Ge [55].

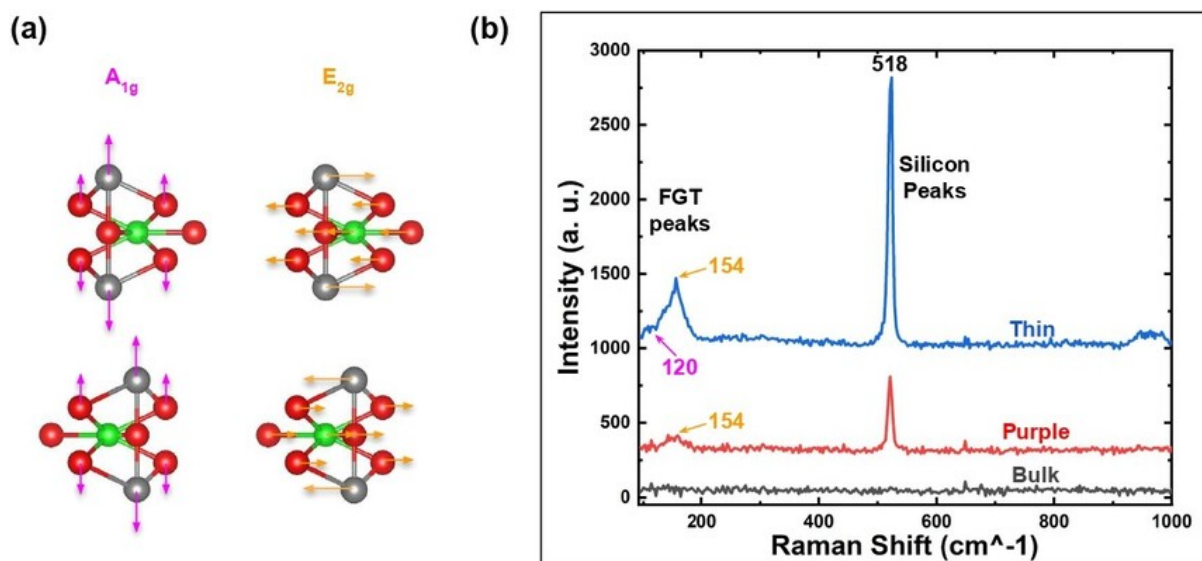


Figure 5.2 | Raman Spectroscopy of Fe_3GeTe_2 . (a-left) Crystal Structure of FGT showing A_{1g} mode with a pink arrow representing the phonon eigenvector. (a-right) Crystal structure of FGT showing E_{2g} mode with an orange arrow representing the phonon eigenvector (b) Raman spectroscopic data of FGT flakes of variable thickness.

Raman spectroscopic measurements were taken in ambient conditions on FGT flakes with variable thickness and are shown in Figure 5.2 (b). The thickness of the flakes was roughly determined from optical contrast and from the intensity of silicon peaks which becomes pronounced as the FGT flake gets thinner. FGT shows characteristic peaks at 154 cm^{-1} and 120 cm^{-1} as can be seen in thin flakes. The intensity of the peaks gets diminished as the thickness of the flake increases which is in line with the reported data [56]. The peak observed at 120 cm^{-1} belongs to A_{1g} mode and the peak at 155 cm^{-1} is from both A_{1g} and E_{2g} modes combined. The thickness dependence of the Raman spectra obtained can be explained by constructive interference between light scattered from different layers of the material [57].

In the case of FGT, the constructive interference gets stronger as the thickness of the exfoliated flakes decreases.

5.3 Fe-Intercalation in FGT

5.3.1 Estimation of Fe Concentration in FGT

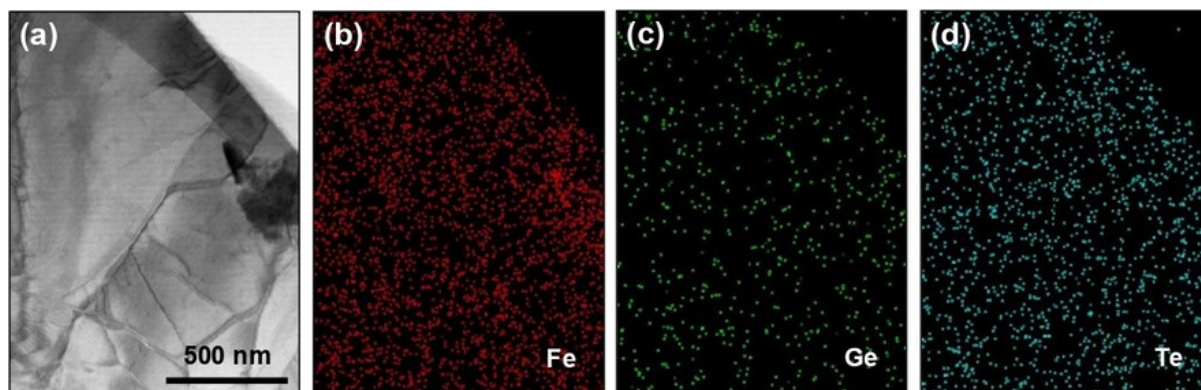


Figure 5.3 | HR-TEM and Elemental Mapping of Fe-intercalated FGT. (a) HR-TEM image of a typical FGT nanoflake. (b) Elemental mapping of Fe. (c) Elemental mapping of Ge. (d) Elemental mapping of Te.

High Resolution - Transmission Electron Microscope was used to characterize FGT crystals with excess Fe concentrations. [Figure 5.3](#) (a) shows the HR-TEM image of one of the exfoliated FGT nanoflakes using the ultrasonication method. Elemental mapping was conducted to extract the stoichiometry of the samples and the results of Fe, Ge, and Te concentrations are shown in [Figure 5.3](#) (b), [Figure 5.3](#) (c), and [Figure 5.3](#) (d) respectively.

	ELEMENTS	Fe	Ge	Te
Sr. No.				
1		3.8	1	1.8
2		4.3	1	1.9
3		5.2	1	1.9
4		3.9	1	1.7

Table 5.1 | HR-TEM and Elemental Mapping of Fe-intercalated FGT. The leftmost column depicts the serial number of the nanoflakes and the topmost row represents the various elements in FGT. The elemental concentration is shown in the table.

Elemental analysis of various flakes was conducted and the results are summarised in [Table 5.1](#). Typical FGT samples have Te vacancies as will be shown in [Chapter 8](#), so stoichiometry was calculated by taking the concentration of Ge to be 1. The resultant Stoichiometry of FGT samples with excess Fe concentrations is determined to be $\text{Fe}_{3+x}\text{GeTe}_2$. Fe concentrations vary roughly from around 3.8 to 5.2 which is explained by possible Fe-intercalation in pristine FGT samples.

5.3.2 Fe-Intercalation in FGT

The excess Fe in FGT can be brought about in two possible ways that are (i) interlayer intercalation which happens in the vdW gap and (ii) Intralayer intercalation in which Fe atoms occupy place inside the layer.

Since pristine FGT has Fe defects as will be shown in [Chapter 8](#), the excess Fe atoms first occupy these sites until the stoichiometry of the sample reaches Fe_3GeTe_2 . Now there are two possible sites where Fe atoms can accommodate as shown in [Figure 5.4](#) (a). Fe atoms can either intercalate on top of Fe II atoms marked as site I or can intercalate on top of Ge atoms marked as site II. Intercalation on site I is more favorable than intercalation on site II and thus the excess Fe atoms sit on top of Fe I, causing a structural change in the material and transforming into Fe_4GeTe_2 . More upcoming Fe atoms occupy site II and after enough intercalation, the structure changes to Fe_5GeTe_2 .

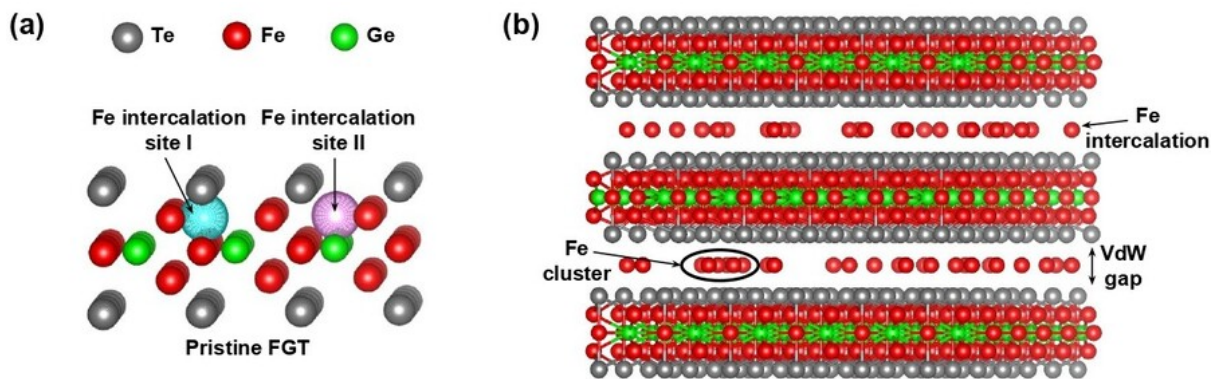


Figure 5.4 | Crystal Structure of Fe-intercalation in FGT. (a) Pristine FGT crystal structure with possible Fe-intercalation sites inside the layer. (b) Crystal structure of Fe-intercalation in interlayer vdW gap.

Another way to accommodate excess Fe atoms is in the vdW gap as was shown in previous reports [58]. Such type of intercalation can be highly non-uniform unlike the intercalation

inside the layer and may form clumps of Fe atoms as shown in [Figure 5.4 \(b\)](#). The thickness of the material can be greatly enhanced depending on the amount of intercalation. Both types of intercalation increase the thickness of the structure with intralayer intercalation having a more subtle effect than the interlayer intercalation which can increase the thickness of one layer up to 0.1 nm.

Intercalation of Fe atoms not only changes the thickness of the sample but can also alter the fundamental physical properties of the sample like magnetism. Recent experiments suggest that the Fe-intercalation in between the layers can lead to antiferromagnetic ordering in the sample [\[58\]](#). Since the paramagnetic-ferromagnetic transition temperature is dependent on Fe atoms, the increase in Fe atoms in the structure causes the transition temperature to increase as iron is ferromagnetic up to 1043 K. This increase in transition temperature is reported to be due to the charge transfer in FGT material [\[59\]](#).

Chapter 6

Surface and Interlayer Oxidation of FGT

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6.1 Oxidation of FGT

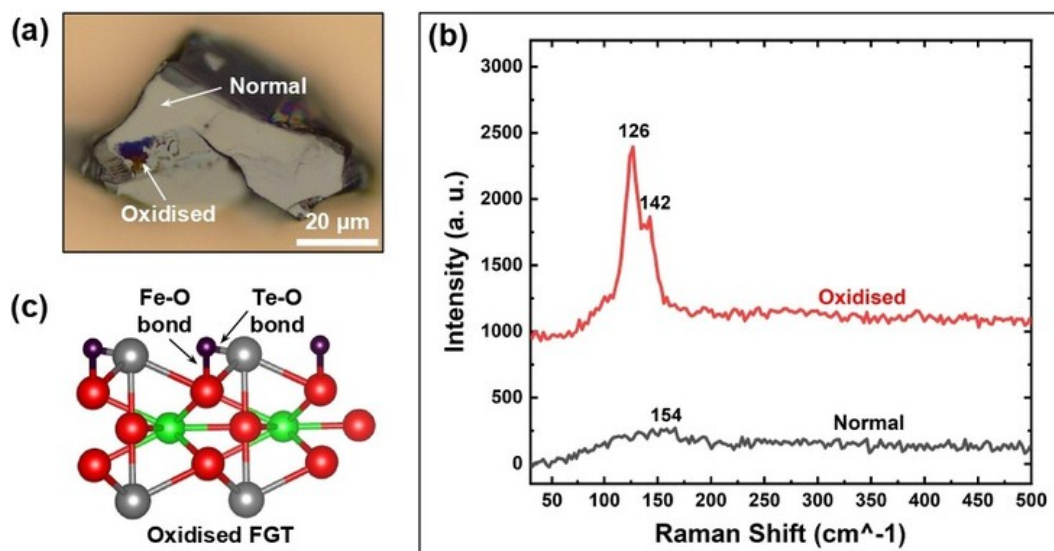


Figure 6.1 | Raman Spectroscopy of Bulk Oxidised FGT Crystal. (a) Optical Microscope image of FGT bulk crystal where the colourful part is oxidized. (b) Raman Spectroscopic data of pristine and oxidized parts as shown in the image (a). (c) Crystal Structure of oxidized FGT layer with Te-O and Fe-O bonds.

The stability of a material is dependent on the strength of its chemical bonds which is determined in terms of cohesion energy E_{coh} [60]. Graphene and hBN are some of the most stable 2D materials and have an E_{coh} greater than 7.0 eV/atom and the E_{coh} of air-sensitive materials are in the range of 3-4 eV/atom. FGT is known to degrade in ambient conditions, but there is no conclusive study on the oxidation of FGT. A detailed study was conducted

using Raman spectroscopy, AFM and transport measurements. Raman spectroscopy is an ideal technique to study the oxidation of FGT as the structural changes occurring due to oxidation can be clearly identified.

Raman Spectroscopy was performed on bulk FGT crystal to characterise the oxidised part. [Figure 6.1](#) (a) shows an FGT bulk crystal where the colourful spot is identified to be oxidised part and the corresponding Raman data are shown in [Figure 6.1](#) (b). Two prominent peaks at 126 cm^{-1} and 142 cm^{-1} can be observed which are reported in the literature to be characteristic peaks of degraded FGT samples [61]. [Figure 6.1](#) (c) shows the crystal structure of oxidized FGT where oxygen forms bonds with iron and tellurium atoms on the surface. These bond formation greatly affects the phonon modes related to Te and Fe I atoms which explains the observed change in raman spectroscopic data where the pristine A_{1g} and E_{2g} modes are suppressed and new modes are observed with the peak observed at 126 cm^{-1} belonging to the E_{2g} mode and the peak observed at 142 cm^{-1} belonging to the A_{1g} mode.

6.2 Surface Oxidation of FGT

6.2.1 Oxidation in Ambient Environment

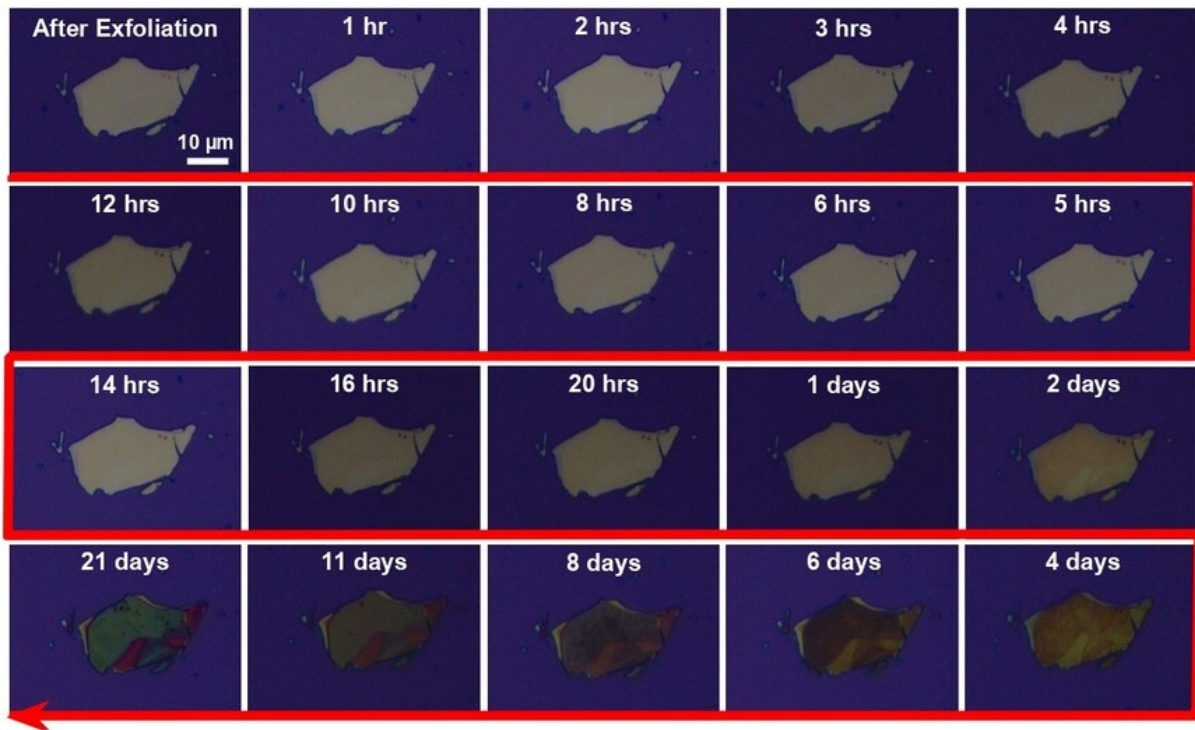


Figure 6.2 | Evolution of Surface Oxidation of FGT. Optical Microscope images of FGT flake taken immediately after exfoliation and up to 21 days. The scale bar is the same for all the images..

FGT crystals were exfoliated and kept in ambient conditions (24°C) to check for the surface oxidation of FGT. Optical microscope images of one of the flakes taken immediately after exfoliation and up to 21 days are shown in Figure 6.2. The characteristic colour of exfoliated bulk flakes is yellow which changes in colour as the surface gets oxidised. Surface oxidation can be seen as the flake changes its colour from yellow to light brown after around 8-10 hours. As the oxidation continues, the surface changes its colour to red as can be seen after 4 days which then changes to green after 21 days where the surface gets completely oxidised.

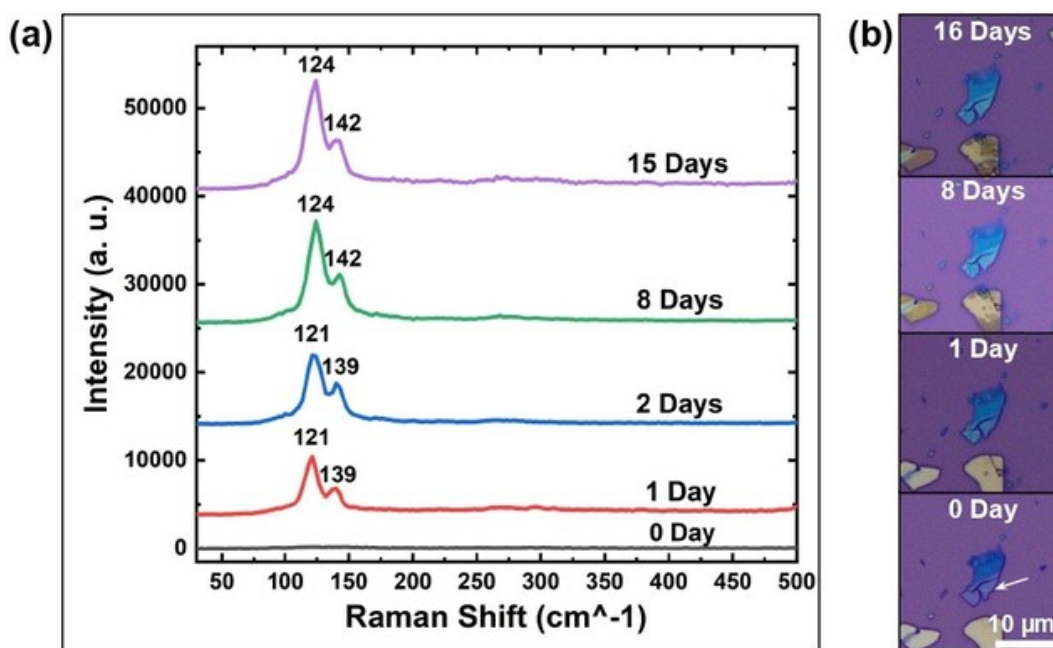


Figure 6.3 | Time Dependent Raman Spectroscopy of FGT Oxidation. (a) Raman Spectroscopic data of exfoliated FGT flake taken immediately after exfoliation and up to 15 days. (b) Optical microscope images of the flake where the marked region shows the area of measurements. The scale bar is the same for all the images.

Raman spectroscopy measurements were performed to check for any structural changes in FGT with respect to oxidation and also relating to the change in contrast of the flakes. Figure 6.3 (a) shows Raman data taken on Bulk FGT flake immediately after oxidation and up to 15 days and the corresponding Optical microscope image of the flake is shown in Figure 6.3 (b). The bulk exfoliated flake shows no prominent peak as noted in Chapter 5, and as the oxidation initializes, two prominent peaks can be observed at 121 cm⁻¹ and 139 cm⁻¹ respectively which then shifts to 124 cm⁻¹ and 142 cm⁻¹ as the surface gets completely oxidized. As the oxidation progresses, the intensity of the Raman peaks can be seen to intensify gradually indicating more Fe-O and Te-O bond formation. The Raman peaks at 121

cm^{-1} and 139 cm^{-1} can be explained as the surface has both the pristine Te and Fe atoms along with the oxidized part. The observed Raman peaks at 124 cm^{-1} and 142 cm^{-1} even after 15 days suggest no structural change in the different contrast observed on FGT flakes.

6.2.2 Oxidation at Higher Temperatures

The rate of oxidation is dependent on various external factors such as temperature and pressure [62]. The oxidation of FGT at 100°C in ambient conditions was reported to oxidize in 30 min [63]. Oxidation of FGT in ambient conditions is termed natural oxidation and at higher temperature ranges as fast oxidation. The oxidation of naturally oxidized FGT was found to have magnetic properties whereas the heated oxidized part is non-magnetic [64].

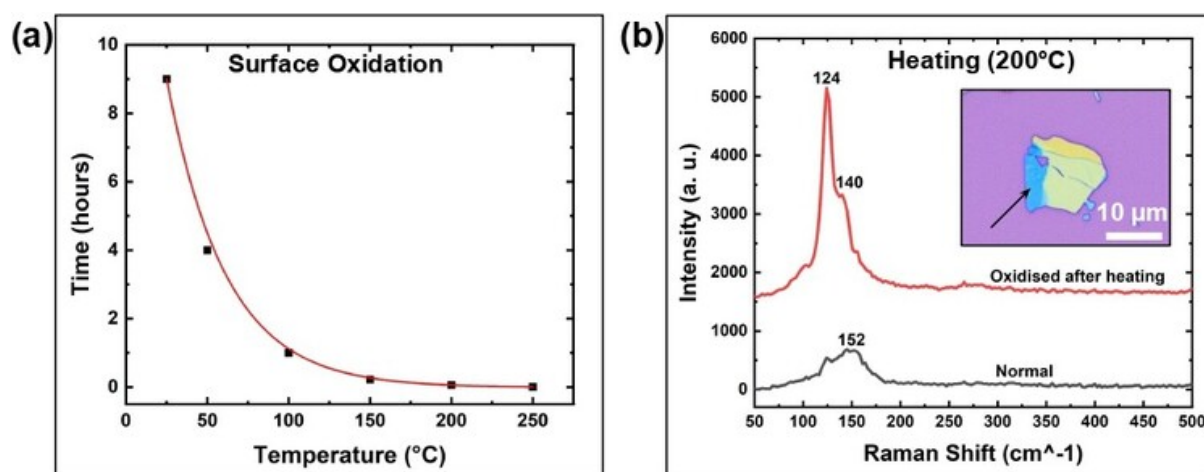


Figure 6.4 | Temperature Dependent Oxidation of FGT. (a) Temperature-dependent rate of surface oxidation of exfoliated FGT flakes. (b) Raman spectroscopic data of an FGT flake before and after heating at 200°C for 10 min. Inset showing the optical microscope image of the flake where the marked region shows the area of measurements.

Oxidation of FGT was studied at different temperature ranges. Figure 6.4 (a) shows the time of onset of surface oxidation with respect to temperature. It was found that the rate of oxidation increases exponentially with temperature. Flakes were oxidized within 15-20 sec at 250°C , approximately 3-5 min at 200°C , around 15 min at 150°C , around 1 hr at 100°C and around 4 hrs at 50°C . The rate of FGT oxidation was found to considerably decreased when the sample was kept in a closed environment. Also, the oxidation of thinner flakes was observed to be faster than bulk flakes. Raman spectroscopy measurements were performed on pristine exfoliated FGT flake and the same flake after being oxidized by heating at 200°C for 10 minutes and are shown in Figure 6.4 (b). The peaks observed are the same as oxidation in

ambient conditions suggesting the same bond formation for fast oxidation as that in naturally oxidised flake.

The rate of reaction is given by Arrhenius equation [65],

$$K = Ae^{-E_{\text{barrier}}/K_B T}$$

where K is the rate of oxidation, A is a pre-exponential term, K_B is the Boltzmann constant, T is the temperature and E_{barrier} is the energy barrier of the oxidation reaction which determines if a given material will oxidize. The values of A and E_{barrier} are calculated to be 18 hours and 0.76×10^{-2} eV respectively. The calculated value of E_{barrier} is less than the value 0.7 eV, above which a material is stable to oxidation at room temperature [66], which agrees with the observation of oxidation of FGT in ambient conditions.

6.2.3 Oxidation-Induced Surface Roughness

As 2D materials are known for their ultra-flat surface, they are used in making heterostructures with superior interface contact [67]. This interface can be substantially hampered if the surface is rough. One of the ways the surface can acquire roughness is surface oxidation.

AFM was used to determine the surface characteristics of exfoliated flakes for up to 30 days. Figure 6.5 (a) shows a 3D view of AFM images taken on exfoliated FGT samples immediately after exfoliation and up to 20 days. It can be clearly observed that the surface gets rough along with oxidation with some regions forming lumps. Surface characteristics were studied on the region marked by a black square and the corresponding graph is shown in Figure 6.5 (b). The average surface roughness of the exfoliated FGT flake is around 0.78 nm in close range of the reported data [68]. The surface roughness increases in a sigmoidal fashion in which the roughness remains unchanged till the onset of oxidation and increases exponentially until reaching saturation after about 20 days with an average surface roughness of about 3.15 nm. The average surface roughness of the flake after 20 days fluctuates around 3 nm.

The inset in Figure 6.5 (b) shows the height profile of the oxidized FGT flake marked by a white-dotted line in the bottom-right image of Figure 6.5 (a). The height of the observed hump is found to be around 37 nm in height which is unusual for surface oxidation and hints at heavy oxygen intercalation in between the layers.

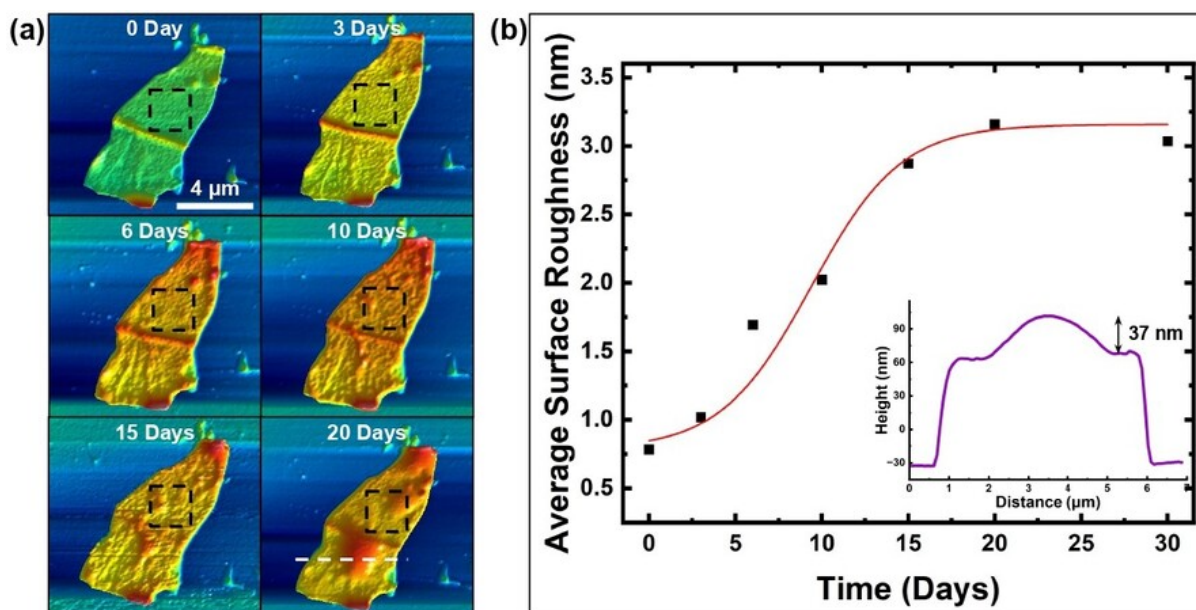


Figure 6.5 | Roughness Analysis of Surface Oxidation of FGT flake. (a) A 3D view of AFM images of FGT flake taken right after exfoliation and up to 20 days. The scale bar is the same for all the images. (b) Time evolution of Average Surface Roughness of FGT flakes kept in ambient conditions. The inset shows the height profile of the bump observed on the oxidized FGT flake after 20 days with the corresponding line scan shown by the white dotted line in the bottommost right image in (a).

6.3 Interlayer Oxidation of FGT

As vdW materials have interlayer spacing that can accommodate different atoms, oxygen intercalation is possible in FGT. The size of molecular oxygen is 0.3 [69] nm which is comparable to the vdW gap in FGT, so the intercalation of oxygen can cause a substantial increase in the thickness of the exfoliated flakes. AFM studies were carried out on FGT flakes to investigate the effect of oxygen intercalation which are shown in Figure 6.6. AFM of FGT was carried out immediately after exfoliation and up to 16 days. The height of the exfoliated flake was determined to be 56 nm. The thickness of the flake remains unchanged until 20 hours and starts to increase thereafter indicating initiation of oxygen intercalation. The thickness rises exponentially up to 10 days and remains constant thereafter indicating a saturation of the intercalation. The evolution of the flake follows a sigmoidal fashion with the final thickness of the flake around 105 nm which is almost double that of the initial flake.

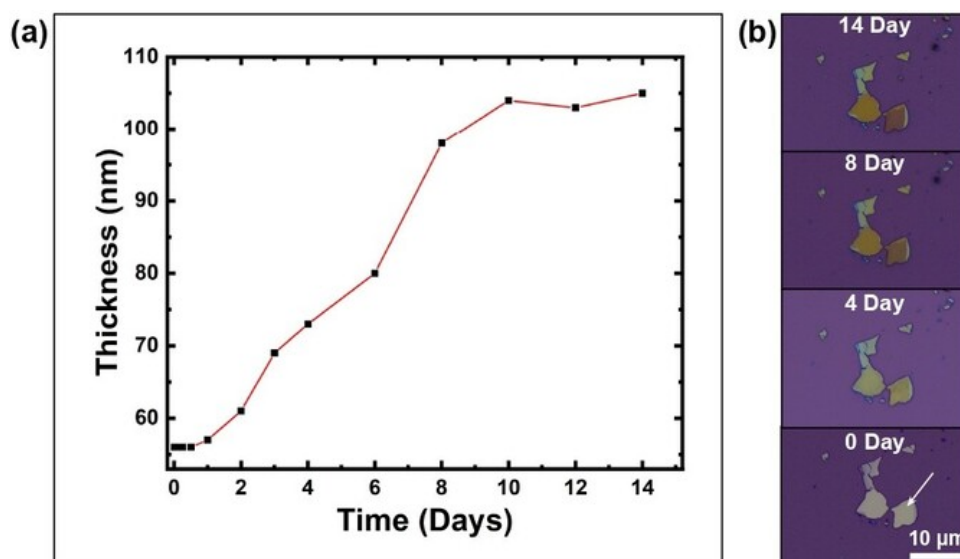


Figure 6.6 | Thickness Evolution of Oxidation of FGT Flake. (a) Thickness evolution of exfoliated FGT flake kept in ambient conditions with time. (b) Corresponding Optical microscope images of the flake. The scale bar is the same for all the images.

Usually, this type of intercalation causes the flake to be cleaved in the vdW gaps known as exfoliation using intercalation [70]. However, the flakes were observed to be quite stable. This suggests that the oxygen atoms are not only intercalated in between the layers but also form bonds inside leading to oxidation inside the vdW gaps. Reports suggest that oxidized FGT creates an interface with the pristine FGT [22,71] which also suggests that the oxidation inside the layers is not caused by the infusion of oxygen atoms from the top surface but by the oxygen that is intercalated in the vdW gaps.

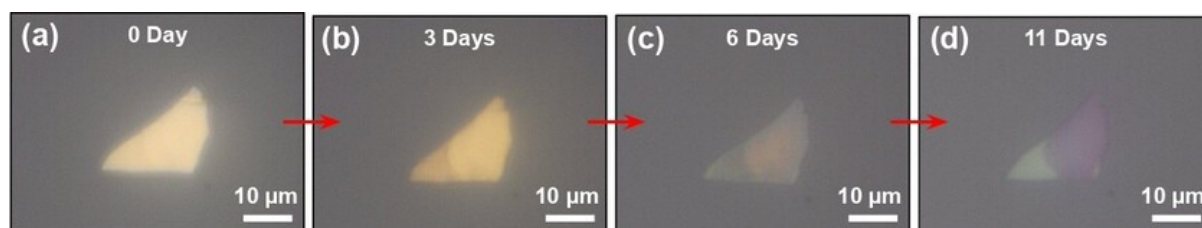


Figure 6.7 | Oxidation of FGT Flake Exfoliated on PDMS. Optical microscope images of FGT flake exfoliated on PDMS taken (a) immediately and after (b) 3 days (c) 6 days and (d) 11 days.

To confirm the hypothesis, FGT flakes were exfoliated on PDMS to check for interlayer oxidation. PDMS acts as a protective layer and its optically transparent property enables it to check for oxidation on the protected side. Figure 6.7 shows optical microscope images of

FGT flakes exfoliated on PDMS taken right after exfoliation and up to 11 days. FGT flakes start to oxidize after about two days on the side that was protected by PDMS suggesting FGT oxidation occurs inside the flakes along with oxygen intercalation.

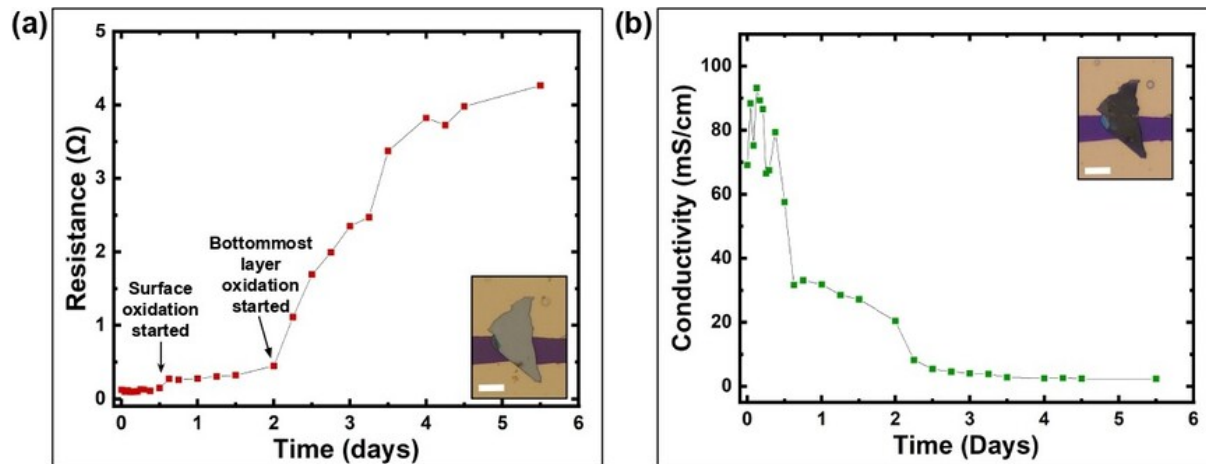


Figure 6.8 | Transport Properties of Oxidising FGT Flakes. (a) Evolution of resistance of FGT flake kept in ambient conditions with time. The inset shows an optical microscope image of the FGT flake just after transferring with a scale bar representing 10 μm . (b) Corresponding electrical conductivity of FGT flake with time. The inset shows an optical microscope image of the FGT flake after 5 days with a scale bar representing 10 μm .

Finally, transport measurements were carried out on FGT flakes to confirm the interlayer oxidation. FGT flakes were exfoliated on pre-patterned contacts and transport measurements were taken right after exfoliation and up to 5 days. Figure 6.8 (a) shows the resistance of FGT flakes with respect to time. The resistance of FGT flakes is fairly constant for up to 10 hours which is the same time as the start of surface oxidation. The resistance starts to increase along with oxidation which is in line with the prevailing knowledge that the oxidised part becomes insulating. There is a kink observed in resistivity values at around 2 days suggesting the bottommost layer in contact with the contacts has started to oxidise. The resistance of flakes increases for up to 4 days and remains fairly constant thereafter. This suggests that enough oxygen molecules are intercalated inside the vdW gaps which restricts the current flow.

Since the thickness of FGT flakes also increases with oxidation, the conductivity values are calculated according to the thickness at the time of transport measurements. The corresponding conductivity values are shown in Figure 6.8 (b).

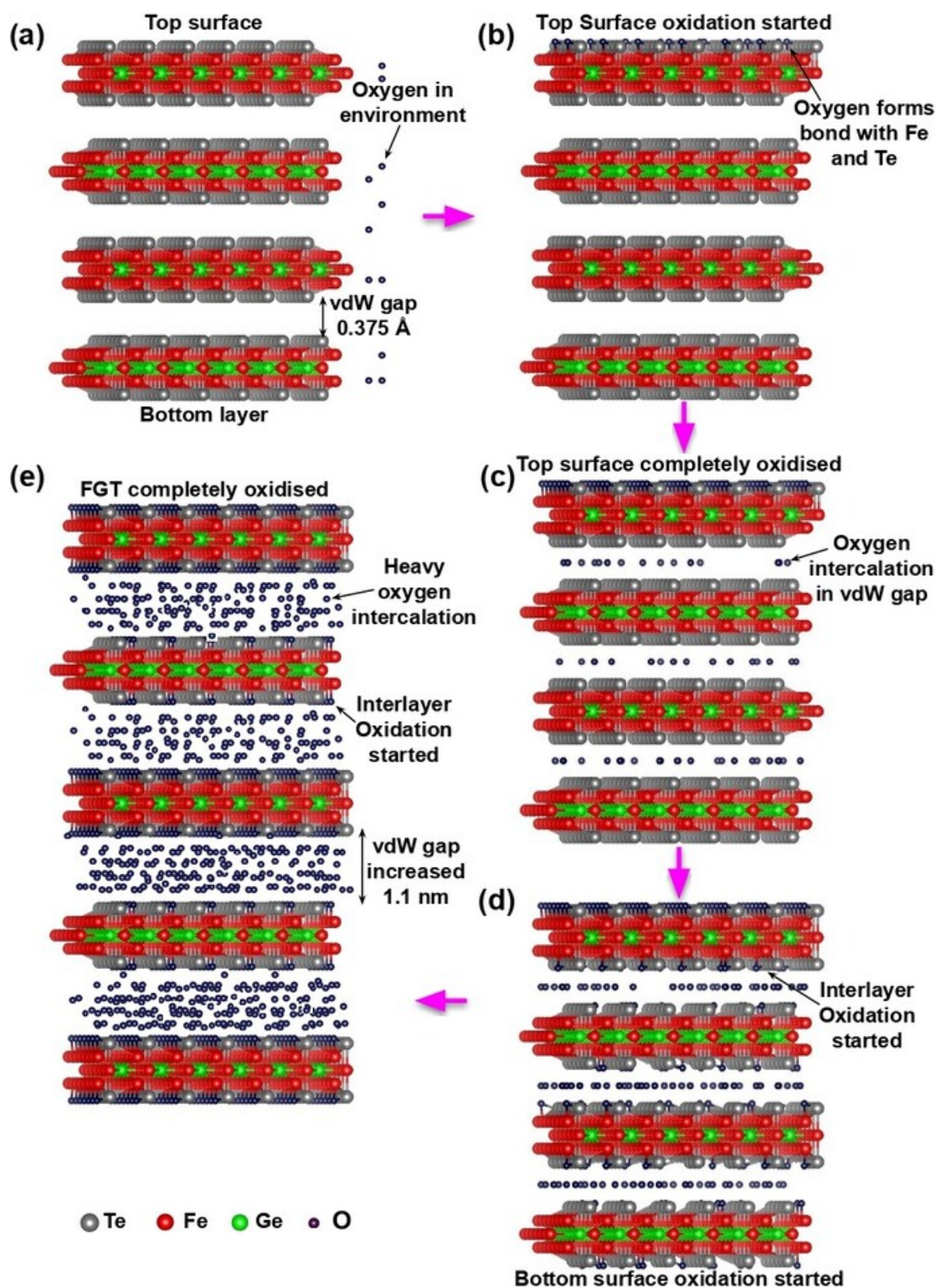


Figure 6.9 | Crystal Structure of Evolution of Oxidation of FGT Flakes. (a) Crystal structure of Pristine FGT flake in ambient conditions. (b) Crystal structure of FGT with surface oxidation initialized after around 8 hours. (c) Crystal structure of FGT with the start of oxygen intercalation in the vdW gap causes its thickness to increase after around 20 hours. (d) Crystal structure of FGT with the start of oxidation of the bottommost layer after around 2 days. (e) Crystal Structure of completely oxidized FGT flake after around 15 days.

The complete process of the oxidation of FGT flakes is shown by the crystal structure in Figure 6.9. Figure 6.9 (a) shows the pristine FGT flake in an ambient environment surrounded by oxygen molecules. Figure 6.9 (b) shows the onset of surface oxidation which is in contact with the environment. Surface oxidation starts at about 8 hrs for bulk flakes. Figure 6.9 (c) shows the onset of oxygen molecule intercalation inside the vdW gaps leading to an increase in the thickness of the layers. Figure 6.9 (d) shows the initialization of the bottommost exfoliated flake that is oxidized along with interlayer oxidation. Figure 6.9 (e) shows the complete oxidation and oxygen intercalation after 10 days.

Thus, FGT exhibits interlayer oxidation in both thin flakes and bulk exfoliated flakes which is contrary to the report that the bulk flake becomes self-protected after initial reactions [72].

Section II

Chapter 7

Setup and Working of LT-STM

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7.1 STM and STS

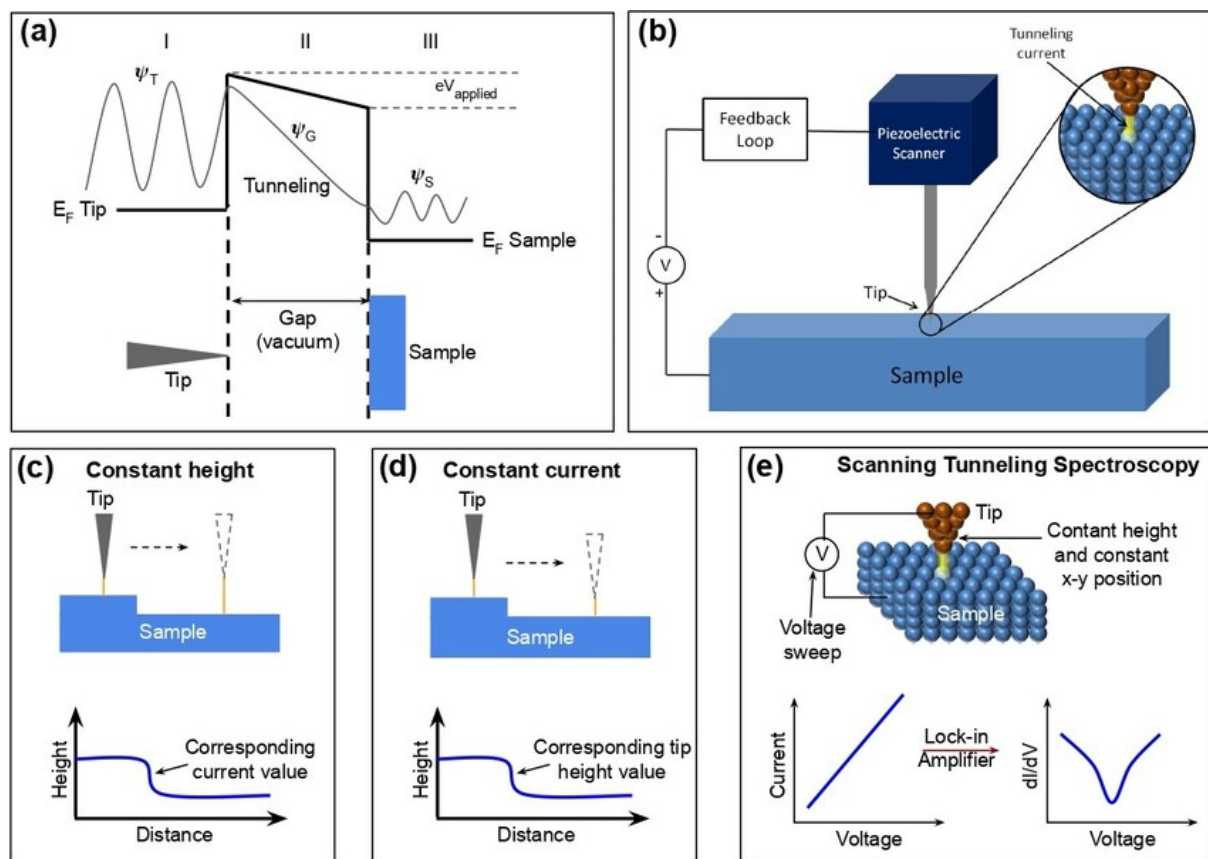


Figure 7.1 | Working Principle of STM and STS. (a) Phenomena of quantum tunneling of electrons. (b) Schematic diagram of the operating principle of STM. (c) Working principle of STM in constant height mode. (d) Working principle of STM in constant current mode. (e) Schematic diagram of the working principle of STS with graphs showing STS of typical metallic samples.

7.1.1 Quantum Tunneling

At the quantum level, electrons behave as a wave that can cross a potential barrier provided enough energy, this phenomenon is known as quantum tunneling. STM works on the principle of quantum tunneling of electrons [73]. The schematic diagram of the same is shown in Figure 7.1 (a). A metallic tip is brought in close proximity to a conducting sample such that electrons are tunneled through the gap (vacuum) which gives rise to a current flow between the tip and sample. The wavefunction of the electron ψ satisfies the Schrodinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

where, $\hbar$ is Planck's constant, m is the mass of the electron, E is the energy of the electron. The solution to this equation is an oscillating wave function in Regions I and III and exponentially decaying in Region II given as follows

$$\text{Region I : } \psi_T = Ae^{ikx} + Be^{-ikx}$$

$$\text{Region II : } \psi_G = Ce^{-\kappa x} + De^{\kappa x}$$

$$\text{Region III : } \psi_S = Ee^{-ikx}$$

$$\text{where, } k^2 = \frac{2m}{\hbar^2} (E - V), \kappa^2 = \frac{2m}{\hbar^2} (V - E),$$

A, B, C, D and E are constants. The gap d between the regions I and III which in the case of STM is the tip-sample distance will determine if the electron tunnels through it.

7.1.2 Scanning Tunneling Microscopy

STM was developed in 1981 by Gerd Binnig and Heinrich and Rohrer [74]. A Schematic diagram of the operating principle of STM is shown in Figure 7.1 (b). A voltage bias is applied to the tip and the sample is grounded. The tip is attached to a piezoelectric scanner and is brought close to the sample in the tunneling range. The tip is then raster scanned on the surface of the sample in the x-y direction. The z-piezo is used to monitor the tip height which is coupled to a feedback loop that monitors the z position of the tip according to the set parameters.

STM works in two modes which are constant height and constant current mode. In constant height mode, the tip height is used as a feedback parameter which is kept fixed while

scanning the sample, and the corresponding change in tunneling current is recorded as an image. Usually, this mode is used for samples that are ultra-flat. In constant current mode, the tunneling current is used as a feedback parameter which is kept constant while scanning the sample, and the corresponding tip height is recorded as an image. All the STM measurements were performed using constant current mode.

7.1.3 Scanning Tunneling Spectroscopy

STS is used to provide information about the density of electrons as a function of their energy. The working of STS is shown in [Figure 7.1 \(e\)](#). The tip is positioned at a particular spot on the sample and a constant height is maintained with the feedback turned off. A sweeping voltage bias is applied to the tip and the corresponding I-V curve is recorded. The $dI/dV - V$ of the curve will be directly proportional to the local density of states (LDOS) of electrons in the region of study which is directly below the tip. Also, a $dI/dV - V$ map can be taken across a particular region to spatially visualize the DOS in the region. Taking the $dI/dV - V$ can be extremely noisy, so a lock-in amplifier was used to extract the data which is explained in [Appendix B](#).

7.2 LT-STM

[Figure 7.1 \(a-b\)](#) shows the Scienta Omicron low-temperature ultra-high vacuum STM where all STM measurements were performed. The system is divided into 3 sections which are the LT-STM chamber, Preparation chamber and load lock, each operating at different vacuum conditions and separated by a valve. Samples and tips are moved across each chamber using a magnetic wobble stick.

7.2.1 LT-STM Chamber

The LT-STM chamber is equipped with a bath cryostat for liquid nitrogen (LN_2) and liquid helium (LHe) which enables the system to work in three different temperature ranges that are 300 K (room temperature), 77 K, and 4.3 K. LT-STM chamber has a base pressure of 2×10^{-9} mbar and can reach up to 10^{-11} mbar. The tip-sample assembly is coupled to a sample holder which is suspended using a spring for vibration isolation. The spring has three possible positions (i) cool-down position in which the assembly is in contact with cryostat, (ii) bakeout position is used when baking the system and (iii) scanning position while taking measurements. The sample holder is equipped with a heater for temperature-dependent measurements.

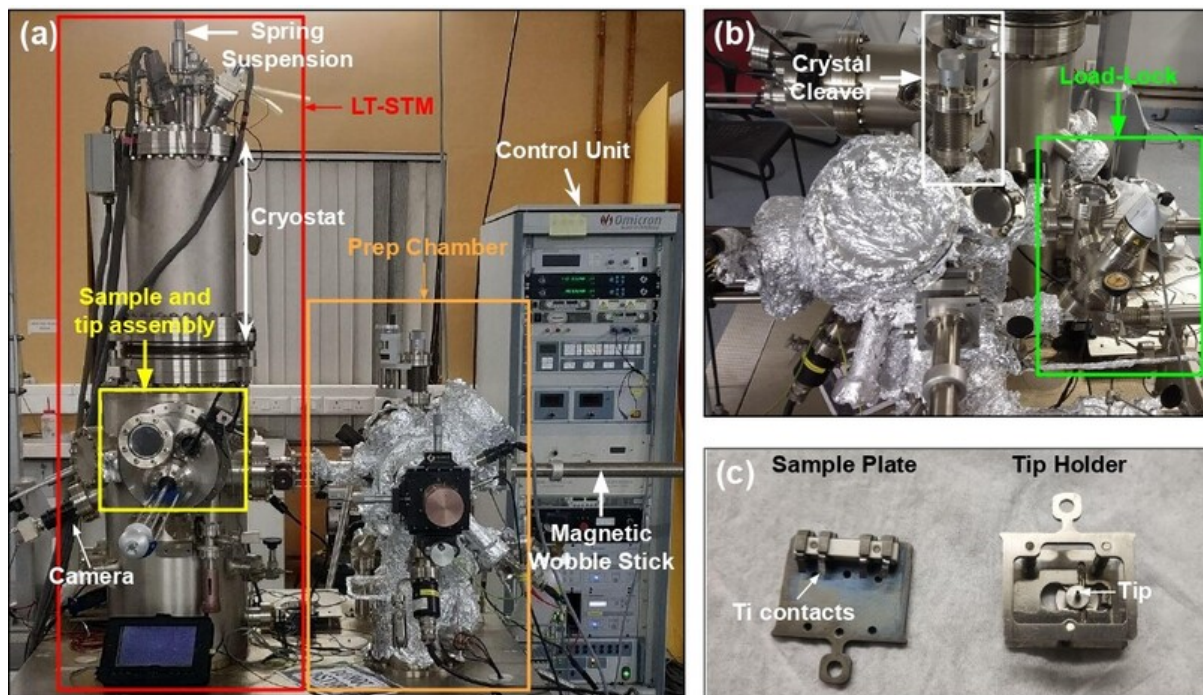


Figure 7.2 | LT-UHV-STM Instrument. (a) LT-STM instrument showing LT-STM chamber, Preparation chamber and control unit along with other components. (b) LT-STM instrument showing load-lock and crystal cleaver. (c) Sample plate and tip holder.

7.2.2 Preparation Chamber and Load Lock

All samples and tips are first transferred into the fast-entry load lock before moving into the preparation chamber. The load lock has a base pressure of 10^{-7} mbar. The preparation chamber is equipped with a sputtering system for cleaning samples and resistive heating for annealing samples. It also has an e-beam evaporator and a crystal cleaver for in-situ exfoliation of samples. The preparation chamber has a base vacuum of 10^{-8} mbar and can reach up to 10^{-10} mbar.

7.2.3 Sample Plates and Tip Holder

Three types of plates are used in the system. (i) sample plate for STM measurements is shown in Figure 7.4 (a), (ii) 4-contact sample plate for transport and tip holder for STM tips. The transport sample plate is equipped with four titanium contacts as shown in Figure 7.2 (c-left). The tungsten tip is attached to the tip holder as shown in Figure 7.2 (c-right) which will be coupled to the piezoelectric scanner in the LT-STM chamber. The tip has a range of 5 x 5 mm for coarse motion and 2 x 2 μ m for fine motion during scanning.

7.2.4 Vacuum Components

Four types of vacuum pumps are used in the system which are rotary pump, turbo-molecular pump, ion pump, and titanium sublimation pump (TSP). The rotary pump creates a rough vacuum of 10^{-3} mbar which is then brought to 10^{-9} mbar using a turbomolecular pump. The ion pump maintains a pressure of 10^{-9} mbar as the turbomolecular pump is switched off during scanning to avoid noise. TSP pump is used at regular intervals to remove the adsorbed gases in the system. LT-STM is connected to one set of the four pumps and the Prep chamber and load lock to another set. Pressure gauges such as the Pirani gauge and ion gauge are used to monitor the pressure. Pirani gauge is used in load lock and ion gauges are used in both prep chamber and LT-STM chamber separately.

7.3 STM Tip Preparation

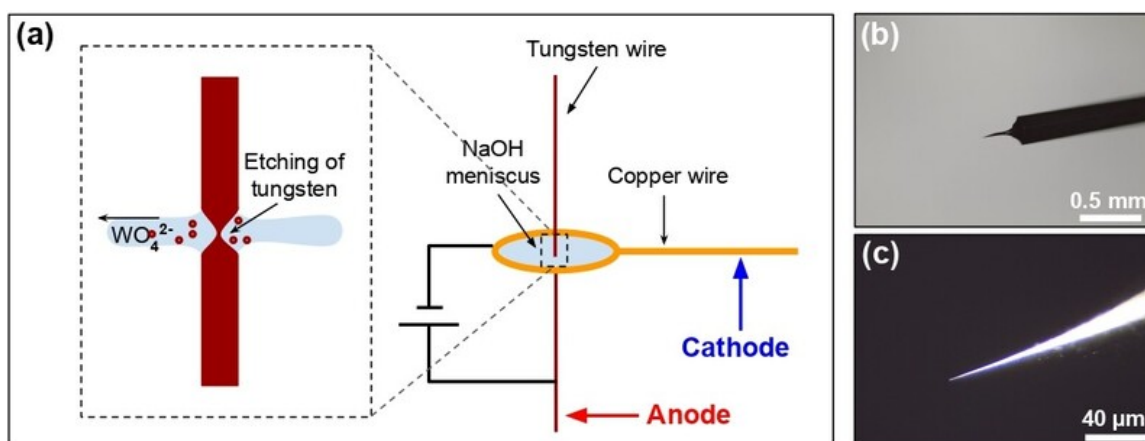


Figure 7.3 | STM Tip Preparation. (a) Schematic diagram of electrochemical etching of STM tungsten tip with magnified part highlighting chemical reaction. (b) Optical microscope image of STM tip(5x magnification). (c) Optical microscope image of STM tip (50x magnification).

Pt/Ir, gold, and tungsten (W) are some common materials used for STM tip preparation. STM tips are made using a wide variety of methods such as mechanical pulling, electrochemical etching, and beam deposition [75]. Direct current electrochemical etching was used to develop tungsten tips. The resolution of the STM image gets better as the tip gets sharper, so the process was optimized to get sharp tips. A tungsten wire of 0.25 mm was used for tip preparation and 2M NaOH solution was used as an electrolyte solution. A Schematic of the tip preparation setup is shown in Figure 7.3 (a). Tungsten wire is dipped in NaOH solution

and positive potential is applied to the wire. A chemical reaction occurs along the meniscus formed and the tip gets etched. The part of the tungsten wire below the meniscus falls down from its weight as the wire gets etched leaving behind a sharp tip. The reaction is as follows

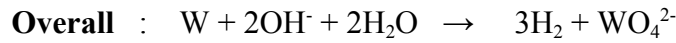
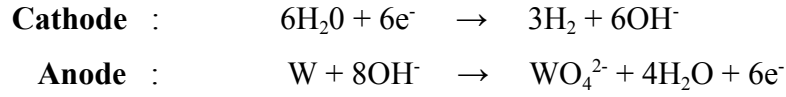


Figure 7.3 (b-c) shows optical microscope images of the STM tips prepared.

7.4 STM Sample Preparation

The STM plate was polished using sandpaper and then sonicated in acetone and then IPA to get a clean and flat surface. FGT bulk crystal was mounted on the STM sample plate using silver epoxy as an adhesive material as shown in Figure 7.4 (a). It was cured at 150°C for 1 hour at a vacuum of 10^{-6} mbar pressure to avoid sample degradation. The top side of the sample was exfoliated using scotch tape, the exfoliated part is shown in Figure 7.4 (b) suitable for STM measurements. The sample was then immediately transferred to the load lock with a base pressure of 10^{-7} mbar as shown in Figure 7.4 (c). The sample was then moved to the prep chamber before transferring into the LT-STM chamber where all the STM measurements were performed at a base pressure of 2×10^{-9} mbar and a temperature of 4.3 K.

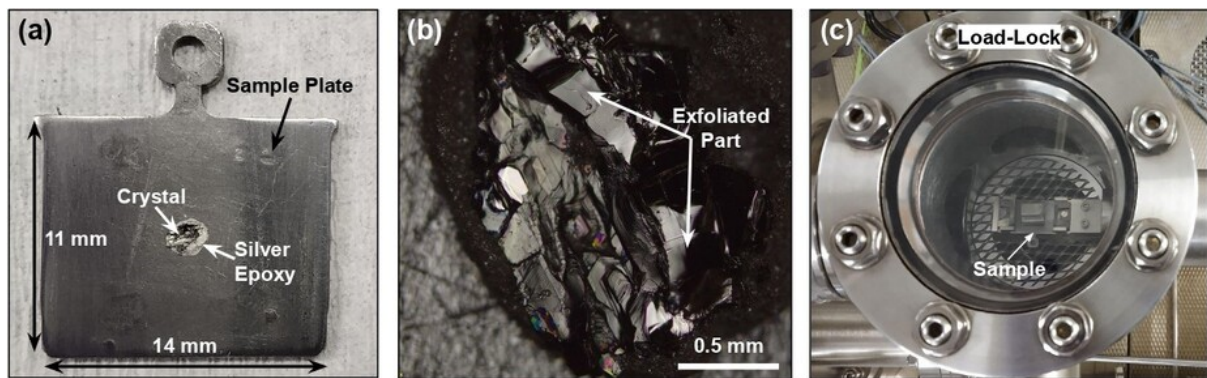


Figure 7.4 | STM Sample Preparation. (a) FGT crystal affixed on STM sample plate. (b) Optical microscope image of FGT crystal after exfoliating top surface. (c) Sample plate along with sample transferred into load lock.

Chapter 8

Defects Study on FGT and Observation of Moiré Pattern

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8.1 Study of Pristine FGT

8.1.1 Topographic Study of Defects

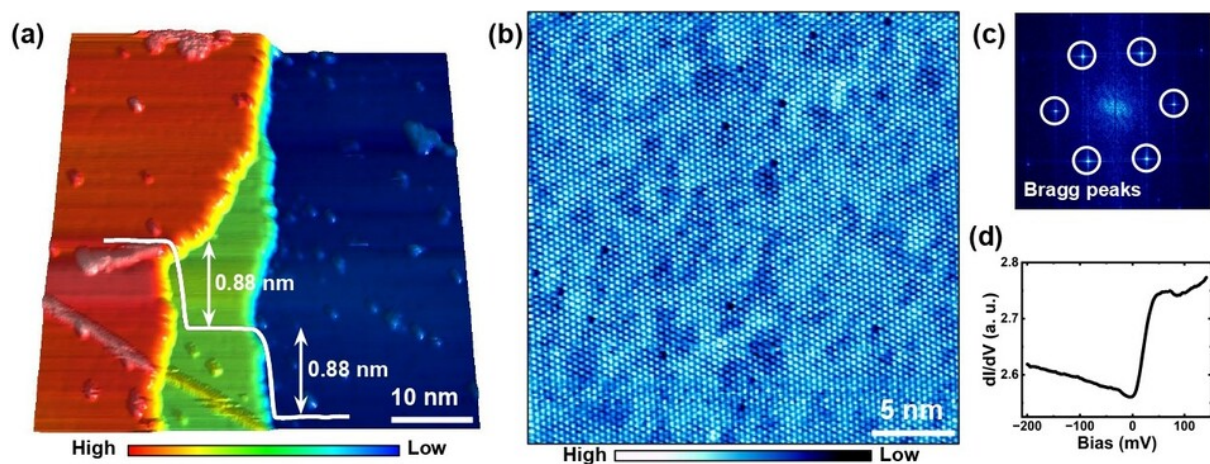


Figure 8.1 | STM of Pristine FGT. (a) A 3D view of a large-scale STM image ($V = 1$ V, $I = 0.1$ nA) of FGT showing a layer cascade with an inset showing the height profile of the layers. (b) STM topographic image ($V = 200$ mV, $I = 50$ pA) of pristine FGT surface. (c) FFT of the image (b) where white circles highlight Bragg peaks. (d) dI/dV spectra taken on the region shown in the image (b).

Figure 8.1 (a) shows a 3D view of a large-scale STM image of the FGT surface showing a layer cascade. The height of a single layer of FGT was calculated to be 0.88 nm which is in line with the reported data [76]. An atomic resolution STM image was taken on a pristine FGT surface and is shown in Figure 8.1 (b). Hexagonal lattice can be clearly seen on the surface which are attributed to Te atoms. Fast Fourier transform of the image shows lattice

peaks (Bragg peaks) which are highlighted in white circles in [Figure 8.1 \(c\)](#). The lattice parameters calculated from the FFT give a lattice spacing between Te atoms to be 0.4 nm. dI/dV spectra taken on the same surface are shown in [Figure 8.1 \(d\)](#). The spectra show two characteristic peaks at 25 mV and -50 mV which are attributed to the Kondo lattice behavior and the paramagnetic-ferromagnetic transition respectively [\[76\]](#).

The surface exhibits many dark spots and a few nanometer-sized regions of subtle depressions which are attributed to the various intrinsic defects and vacancies that are characteristic of the sample [\[77\]](#). The dark spots are due to Te vacancies and the broader low contrast regions are due to the vacancy of Fe I, Fe II, or a combination of both of them.

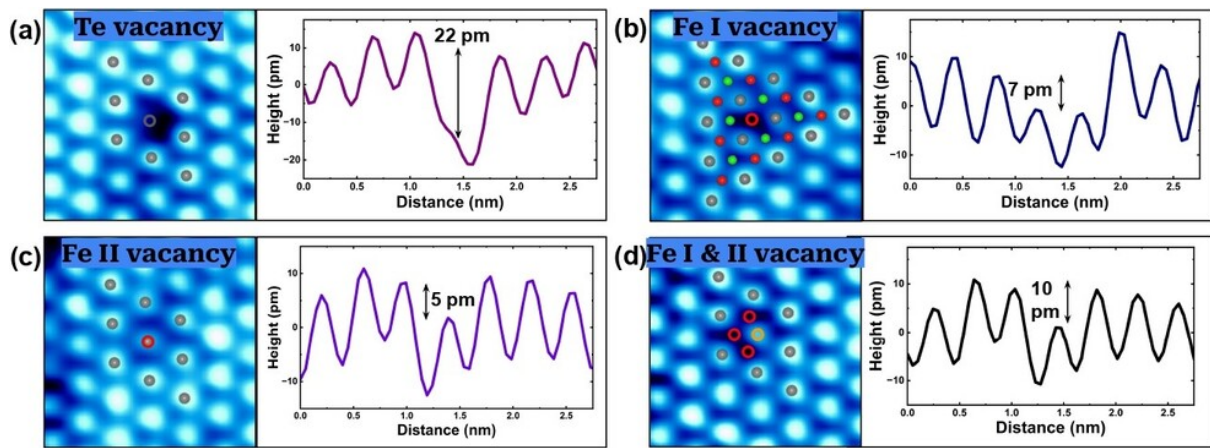


Figure 8.2 | Vacancies in Pristine FGT. (a) Te atoms (grey balls) and Te vacancy (grey circle). (b) Fe I vacancy (red circle) in between three Te atoms (grey balls). (c) Fe II vacancy (red circle) which is right under the Te atom. (d) Fe I and Fe II vacancies are highlighted in red and orange circles respectively.

A detailed study of the vacancies was performed to identify and locate various types of defects in the sample. FGT exhibits three types of atomic deficiency that are Te vacancy, Fe I vacancy, and Fe II vacancy. [Figure 8.2 \(a\)](#) shows an image containing Te vacancy which is identified as a dark spot highlighted by a grey circle in the image and surrounded by Te atoms highlighted by grey balls. The calculated height difference is around 22 pm. [Figure 8.2 \(b\)](#) shows an image containing Fe I vacancy which is marked by the red circle in the image. Fe I is located in between three Te atoms and its vacancy causes a subtle depression on the surrounding Te atoms which can be identified as the surrounding three Te atoms have lower contrast as compared to other Te atoms. The calculated height difference is found to be 7 pm. [Figure 8.2 \(c\)](#) shows Fe II vacancy highlighted as a red circle. Fe II sits directly below the Te atom and its vacancy causes lower contrast on the Te atom at the top which can be clearly

seen in the image. The calculated height difference is 5 pm which is less than the Fe II vacancy as Fe I is a layer below Fe II. Finally, both Fe I and Fe II vacancies were located and are shown in Figure 8.2 (d) which are highlighted in red and orange circles respectively. The calculated height difference of the Te atom on top of these vacancies is found to be 10 pm which is more than that caused by Fe I and Fe II separately.

8.1.2 Spectroscopic Study of Defects

Figure 8.3 (a) shows a linear density of states (LDOS) map taken on the entire region shown in Figure 8.1 (b) at a voltage bias of 25 mV. The regions having Fe vacancies can be clearly seen to have more DOS than the pristine regions. To study the effect of Fe vacancy in detail, STM was carried out on a region where these vacancies can be prominently seen.

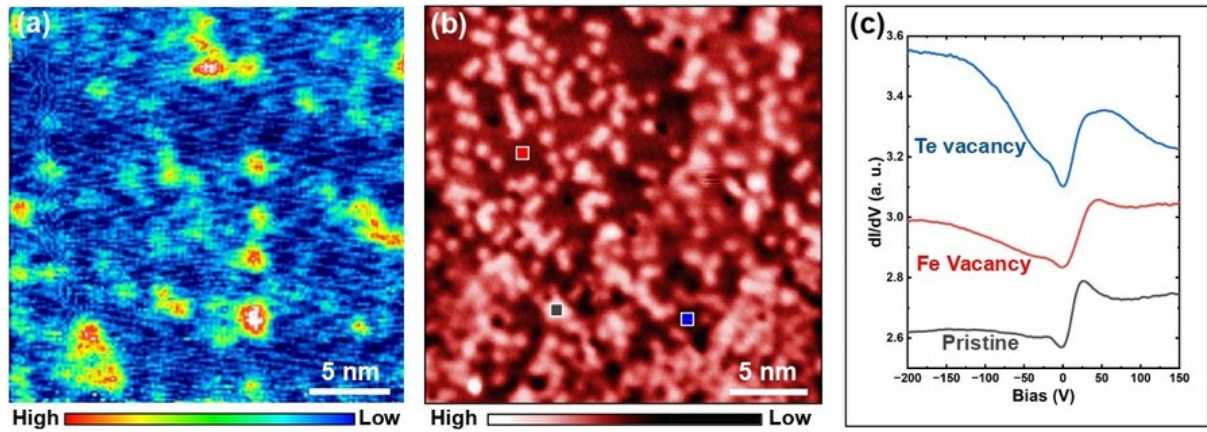


Figure 8.3 | STS of Pristine FGT. (a) LDOS map ($V = 200$ mV, $I = 0.6$ nA) taken on the entire region shown in Figure 8.1 (b) at a bias voltage of 25 mV. (b) High contrast STM image of pristine FGT surface. (c) dI/dV spectra taken at pristine, Fe vacancy, and Te vacancy shown in the image (b) with grey, red, and blue squares respectively.

Figure 8.3 (b) shows a high contrast STM image of the Pristine FGT surface where the bright regions represent pristine FGT surface, darker regions show Fe vacancy, and dark spots show Te defect. Spectroscopic studies were performed on three regions, (i) pristine, (ii) Fe vacancy, and (iii) Te along with Fe vacancy regions marked by grey, red, and blue squares respectively, and the corresponding dI/dV spectra are shown in Figure 8.3 (c). The paramagnetic-ferromagnetic transition peak at -50 mV broadens as we go from region (i) towards region (iii) which can be explained by the decreased Fe content in the region which is the main contributor to the transition. The Kondo lattice peak broadens as we go from region (i) to region (iii) indicating a weakening of the effect. This is evident as the

phenomena arise due to the delocalized d-orbital electrons of Fe [76]. Thus the coexistence of ferromagnetism and Kondo lattice behaviour is confirmed which depends on the Fe concentration in the region.

8.2 Moiré Pattern in FGT

Figure 8.4 (a) shows an STM image of FGT where large-scale periodic modulations can be observed. These patterns have been inferred to be moiré pattern considering the large-scale modulations and the periodicity it exhibits [78]. A 3D view of the same image is shown in Figure 8.4 (b) where the height of the pattern is found to be 35 pm. The periodicity of the pattern was found to be $7.5a_0$ and $15a_0$ giving it the representation of $7.5a_0 \times 15a_0$, where a_0 is the lattice constant. dI/dV spectra taken on the region is shown in Figure 8.4 (c) where the characteristic peaks of pristine FGT are absent and the surface exhibits normal metallic behavior.

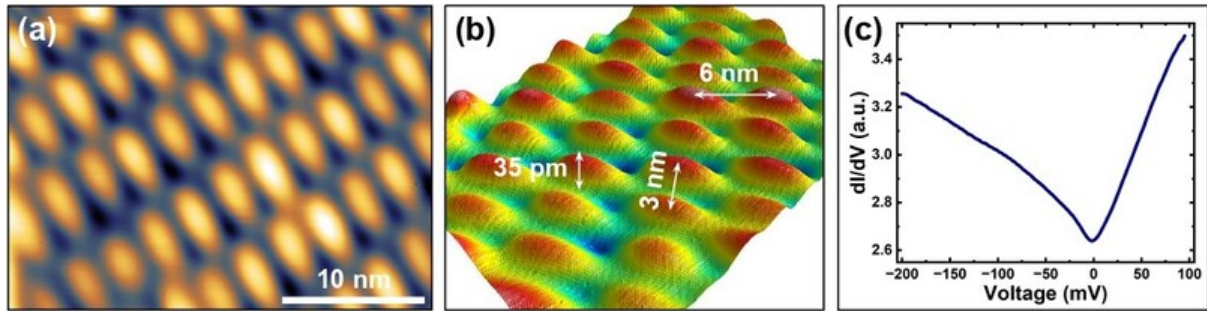


Figure 8.4 | Moiré Pattern in FGT. (a) Large scale STM image ($V = -200$ mV, $I = 0.2$ nA) of moiré pattern on FGT surface. (b) A 3D view of the STM image showing the periodicity of the pattern. (c) dI/dV spectra taken on the same region.

Chapter 9

Charge Ordering in Fe-intercalated FGT

9.1 $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ Charge Ordering in Intralayer Fe-Intercalated FGT	59
9.2 Pristine and $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ Charge Ordering in Intralayer Fe-Intercalated FGT	61
9.3 $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ and $2a_0 \times a_0$ Charge Ordering in Interlayer Fe-Intercalated FGT	63

9.1 $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ Charge Ordering in Intralayer Fe-Intercalated FGT

Intercalation of various elements in vdW materials can change the physics of the materials such as intercalation of Cu in TiS_2 leads to $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ structural transition [79]. In a similar way, the intercalation of Fe inside FGT can alter the physics of pristine FGT. The intercalation of Fe has already been shown in Chapter 5, now we look at its surface properties using STM and STS.

Figure 9.1 (a) shows the STM image of the FGT surface. There are very few Fe vacancies which suggests that Fe has intercalated inside the layer and the surface being very flat rules out the possibility of Fe intercalation in the vdW gap. So the FGT surface exhibits a stoichiometry of $\text{Fe}_{3+x}\text{GeTe}_2$ with intralayer Fe intercalation. Large-scale modulations can be observed on the surface which are identified as charge ordering as will be discussed later. The height profile of the modulation is shown in Figure 9.1 (b) and the corresponding line scan is shown by the blue dotted line in Figure 9.1 (a). Modulations can be clearly seen in the height profile where modulated Te atoms have more height than others in a periodic arrangement. The FFT of the image is shown in Figure 9.1 (c) where Bragg peaks are highlighted in white circles. Orange circles highlight the modulated peaks and the periodicity was determined to be $\sqrt{3}$ times that of the lattice constant a_0 and rotated in 30° with the lattice direction giving them the notion of $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$.

Spectroscopic studies were carried out to characterize the sample along with the features observed and the corresponding dI/dV spectra is shown in Figure 9.1 (d). The spectra is different from that observed in pristine FGT and show a gap with FWHM calculated to be

around 46 mV. The gap opening shows a kind of symmetry breaking and the system assumes lower energy which is attributed to the formation of charge ordering.

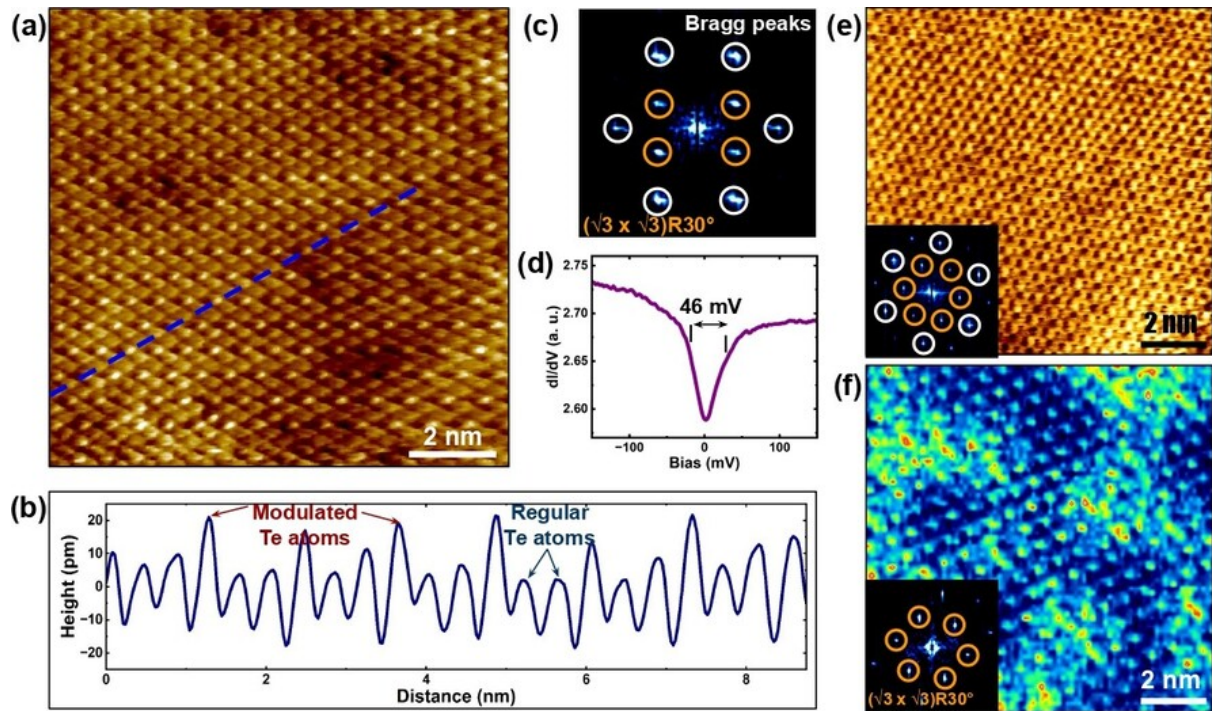


Figure 9.1 | $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ Charge Ordering in Intralayer Fe-intercalated FGT. (a) A STM image ($V = -50$ mV, $I = 0.5$ nA) of $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulated surface. (b) Height profile along one of the lattice directions where the modulated Te atoms can be identified clearly and the corresponding line scan shown by the blue dotted line in the image (a) (c) FFT of the image (a) where orange and white circles highlight the $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulated peaks and Bragg peaks respectively (d) dI/dV spectra taken on region shown in the image (a). (e) An STM image ($V = -200$ mV, $I = 0.1$ nA) of $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulated surface with inset showing FFT of the image. (f) LDOS maps ($V = 200$ mV, $I = 0.6$ nA) taken on the region shown in the image (e). Inset showing FFT of the image with orange circles highlighting $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulated surface.

Figure 9.1 (e) shows an STM image of a different region which is also deduced to have intralayer Fe intercalation. $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulations can be observed on the surface and is highlighted in the FFT taken on the same region as shown in the inset. Spectroscopic studies were performed on the entire region to study the properties of the modulations and the corresponding LDOS map taken at 0 V is shown in Figure 9.1 (f). The modulation is clearly seen in the LDOS maps at the Fermi level and is confirmed by the FFT of the image shown in the inset. This indicates an increase in the DOS on the modulated Te atoms around the Fermi level.

$(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulation has been observed in other FGT systems such as $\text{Fe}_{5-x}\text{GeTe}_2$ [80] where the transition to the modulation was observed below a critical temperature T_{c2} which was accompanied by a weakening of the magnetization in the sample [81]. A more recent theoretical study shows that the structural transition is caused by the Fe I split sites in Fe_5GeTe_2 . The vacancy at these Fe I sites causes the swapping of the Fe I atoms leading to the observed modulation [82]. Here, we show that the modulation can be brought about by doping Fe atoms in pristine FGT with Fe intercalating inside the layers.

9.2 Pristine and $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ Charge Ordering in Intralayer Fe-Intercalated FGT

9.2.1 Topographic Study of Charge Ordering

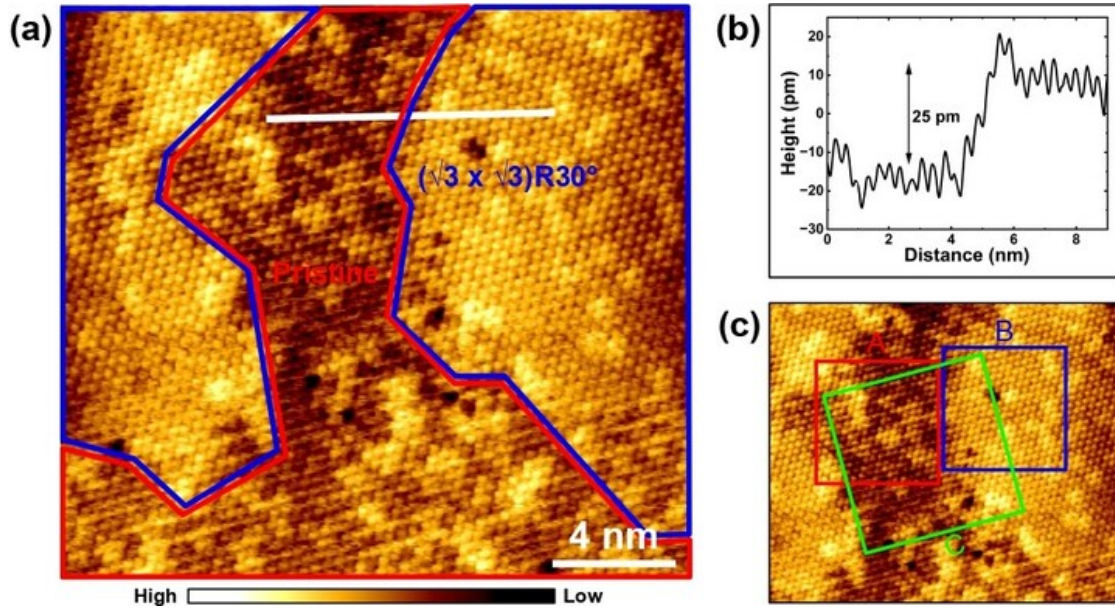


Figure 9.2 | $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ Charge Ordering and Pristine Region. (a) An STM image ($V = -200$ mV, $I = 25$ pA) of $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulated surface highlighted by blue polygon (bright region) and pristine surface highlighted by red polygon (dark region). (b) Height profile of the bright region with the corresponding line scan shown by the white line in the image (a). (c) Zoomed-in image of the region shown in the image (a) with pristine, $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulated and coexisting region marked by red, blue, and green squares respectively.

Figure 9.2 (a) shows STM image of FGT surface where the coexistence of $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulation and pristine lattice can be clearly observed. The region highlighted in red is pristine which can be deduced from the surface inhomogeneity. The surface highlighted in blue is the intralayer Fe-intercalated region which is confirmed by the fact that it shows very

little topographic inhomogeneity. Further, the pristine region has a lower contrast than the intercalated region with a height difference of around 25 pm as shown in the height profile in Figure 9.2 (b) and the corresponding line scan is shown by the white line in Figure 9.2 (a). The measured height difference can be attributed to Fe-intercalation inside the layer.

The region highlighted in blue has a modulation of $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ which is the same as observed previously. To study the various different regions in detail STM measurements were performed in three different regions that are pristine, modulated and region containing both. Figure 9.2 (c) shows the zoomed-in image of Figure 33 (a) with the red marked region being pristine, the blue region is $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulated and the green region with both regions coexisting. Such coexisting regions have been reported in the literature in $\text{Fe}_{5-x}\text{GeTe}_2$ and is attributed to the Fe I atoms [83].

9.2.2 Spectroscopic Study of Charge Ordering

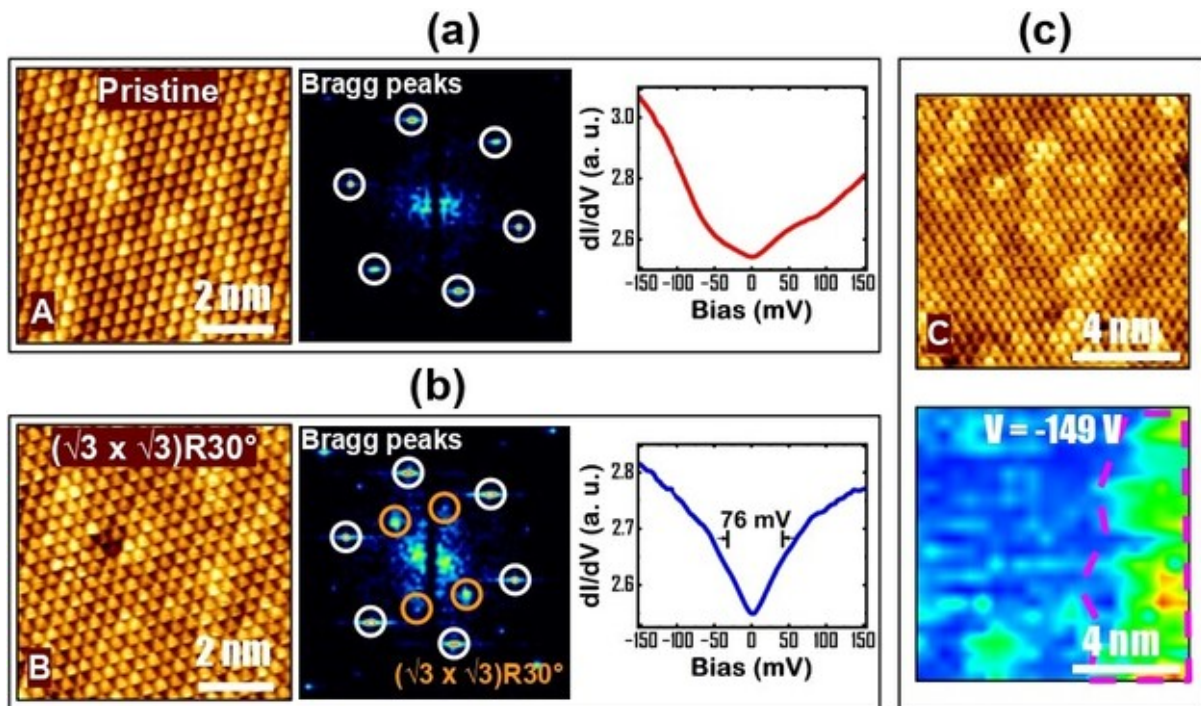


Figure 9.3 | Pristine, $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ and Coexisting Region. (a) Left - A STM image ($V = -200$ mV, $I = 0.1$ nA) of the region A in Figure 9.2 (c), Middle - FFT of the same image, and Right - dI/dV spectra taken on the same region. (b) Left - A STM image ($V = -200$ mV, $I = 0.1$ nA) of the region B in Figure 9.2 (c), Middle - FFT of the same image, and Right - dI/dV spectra taken on the same region. (c) Top - A STM image ($V = -250$ mV, $I = 0.1$ nA) of the region C in Figure 9.2 (c), Bottom - LDOS map on the same region with region marked in pink is $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulated.

Figure 9.3 (d-left) shows the STM image of the region marked by red in Figure 9.2 (c). The FFT of the image is shown in Figure 9.3 (d-middle) which shows only Bragg peaks confirming the region to be pristine. dI/dV spectra taken on the same region is shown in Figure 9.3 (d-right) and show characteristics similar to the pristine with a very broad fano resonance peak which may be due to the competition between pristine and modulated regions. Figure 9.3 (e-left) shows the STM image of $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulated region marked by blue in Figure 9.2 (c). FFT of the image is shown in Figure 9.3 (e-middle) where white circles and orange circles represent Bragg peaks and $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulation peaks respectively. Figure 9.3 (e-right) shows dI/dV spectra taken on the same region which shows characteristics similar to the $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulated region shown in Figure 9.3 (a). The gap was found to be 76 mV which is greater than that observed for purely modulated regions which may again be attributed to the competition between pristine and modulated regions.

Figure 9.3 (f-top) shows the STM image of the region marked by green in Figure 9.2 (c). To study the characteristics of the two regions, LDOS maps were taken at -149 V on the entire region and are shown in Figure 9.3 (f-bottom). The pink dotted region highlights the $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulated surface which has more DOS than the pristine region away from the fermi level indicating possible contributions from the excess Fe atoms.

9.3 $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ and $2a_0 \times a_0$ Charge Ordering in Interlayer

Fe-Intercalated FGT

9.3.1 Topographic Study of Two Types of Charge Ordering

Figure 9.4 (a) shows STM image of FGT surface showing coexisting $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ and a stripe-like modulation. The region highlighted in red shows $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulation and the region highlighted in cyan shows stripe-like modulation. Te and Fe vacancies can be observed throughout the surface which are a characteristic feature of Fe_3GeTe_2 . Large scale modulations can be observed on the surface which is due to Fe-intercalation in between the layers in the vdW gap which will be explained later. So the stoichiometry of the sample is deduced to be $\text{Fe}_{3+x}\text{GeTe}_2$ with the excess Fe atoms in vdW gap.

FFT of the image is shown in Figure 9.4 (b-left) where white circles highlight Bragg peaks and red circles show $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulation. The modulation shown in cyan has a periodicity of 2 times lattice constant a_0 along one of the lattice directions giving it the notion

of $2a_0 \times a_0$ modulation. Spectroscopic study was carried out on the region and the corresponding dI/dV spectra is shown in Figure 9.4 (b-right). It has the characteristics same as the modulated region studied previously and the gap was found to be around 65 mV.

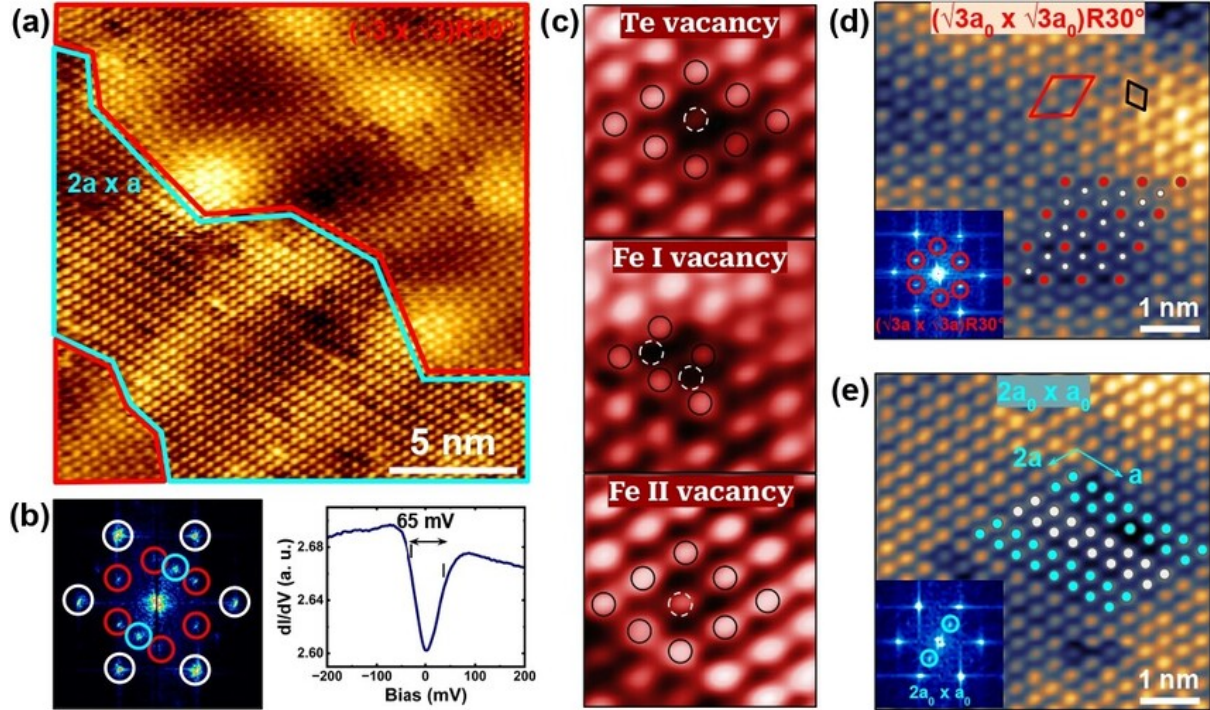


Figure 9.4 | $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ and $2a_0 \times a_0$ modulated Region. (a) An STM image ($V = -100$ mV, $I = 0.1$ nA) of $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulated region shown in red polygon and $2a_0 \times a_0$ modulated region shown in cyan polygon. (b) Left - FFT of the image in (a) with white, red, and cyan circles representing Bragg peaks, $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulated peaks and $2a_0 \times a_0$ modulated peaks respectively. Right - dI/dV spectra taken on the same region (c) Top - Te vacancy (white dotted circle), Middle - Fe I vacancy (white dotted circle) and Bottom - Fe II vacancy (white dotted circle), black circles highlighting Te atoms. (d) An STM image ($V = -200$ mV, $I = 0.1$ nA) of $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulated region showing the unit cell of the modulated part in red polygon and normal lattice in black. The inset shows the corresponding FFT. (e) An STM image ($V = -200$ mV, $I = 0.1$ nA) of $2a_0 \times a_0$ modulated region. The inset shows the corresponding FFT.

Figure 9.4 (c) shows a zoomed-in image of Figure 9.4 (a) displaying the three types of vacancies. The top panel shows Te vacancy which is highlighted as a white dotted circle and can be seen as a black spot on the image. Surrounding Te atoms are highlighted in black circles. The middle panel shows many Fe I vacancies with two of them highlighted with a white dotted circle and can be seen as darker regions on the surface. Fe I causes the surrounding Te atoms to have a subtle depression as can be seen with the lower contrast of

the Te atoms highlighted in black circles. The bottom panel shows Fe II vacancy which is highlighted in a white dotted circle which creates a depression on the Te atom that sits right on top of it causing lower contrast on the Te atom.

Figure 9.4 (d) shows an STM image of $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulated region where the black polygon shows a unit cell of pristine lattice and the red polygon shows the modulated lattice. The inset shows the FFT of the image where modulated peaks are highlighted in red. Te atoms are shown in grey balls with modulated Te atoms in red. Figure 9.4 (e) shows $2a_0 \times a_0$ modulated region with the inset showing FFT of the image where modulated peaks are highlighted in cyan color. The Te atoms are highlighted in cyan and white balls with $2a_0$ periodicity.

9.3.2 Interlayer Fe-Intercalation

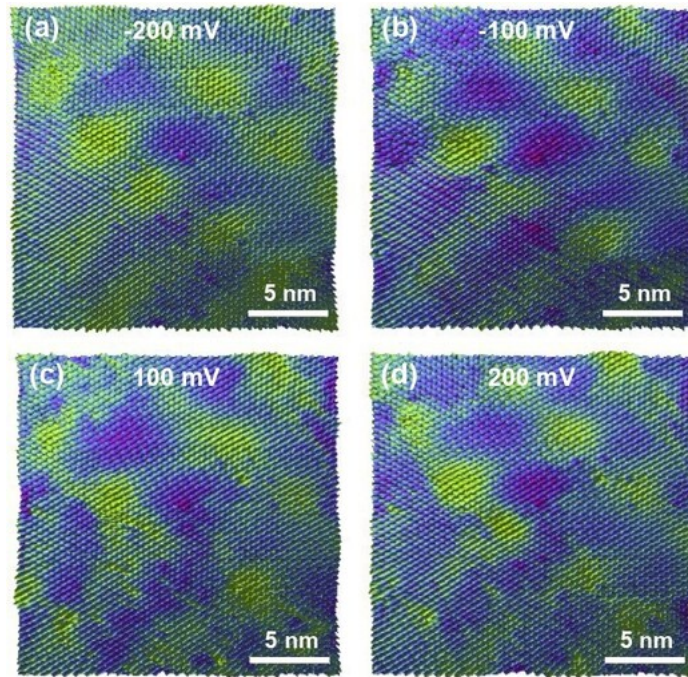


Figure 9.5 | Voltage Dependent STM Imaging. A 3D view of STM images of $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ and $2a_0 \times a_0$ modulated region taken at voltage bias of (a) -200 mV (b) -100 mV (c) 100 mV and (d) 200 mV and tunneling current of 0.1 nA.

The possibility of the large-scale modulation being a moiré pattern is ruled out as there is no periodicity to it. The height profile of the modulation is shown in Figure 9.6 (b) with the corresponding line scan shown in Figure 9.6 (a). The height of the modulation is calculated to be around 100 pm. The surface is not flat and such height variation is due to Fe-intercalation

in the vdW gap where Fe can form clusters as shown in the crystal structure in Figure 5.4 (b). Such a type of intercalation is explained in detail by Laipan et al. [84]. Figure 9.5 (a-d) shows a 3D view of STM images taken on the region at different voltages of -200 mV, -100 mV, 100 mV and 200 mV. The modulation is found to change its shape at different voltages providing further evidence that it is not structural ruling out Fe-intercalation inside the layers.

9.3.3 Spectroscopic Study of Two Types of Charge Ordering

Spectroscopic studies were performed on the region to check any difference in the properties of the two regions. LDOS maps were taken at voltages of 1 mV and 150 mV and are shown in Figure 9.6 (c) and Figure 9.6 (d) respectively. The region marked by the red dotted line in Figure 9.6 (c) shows $2a_0 \times a_0$ modulated region which shows lower Density of State (DOS) values around the fermi level. There is no considerable change in DOS away from the fermi level as evident from the map at 150 mV.

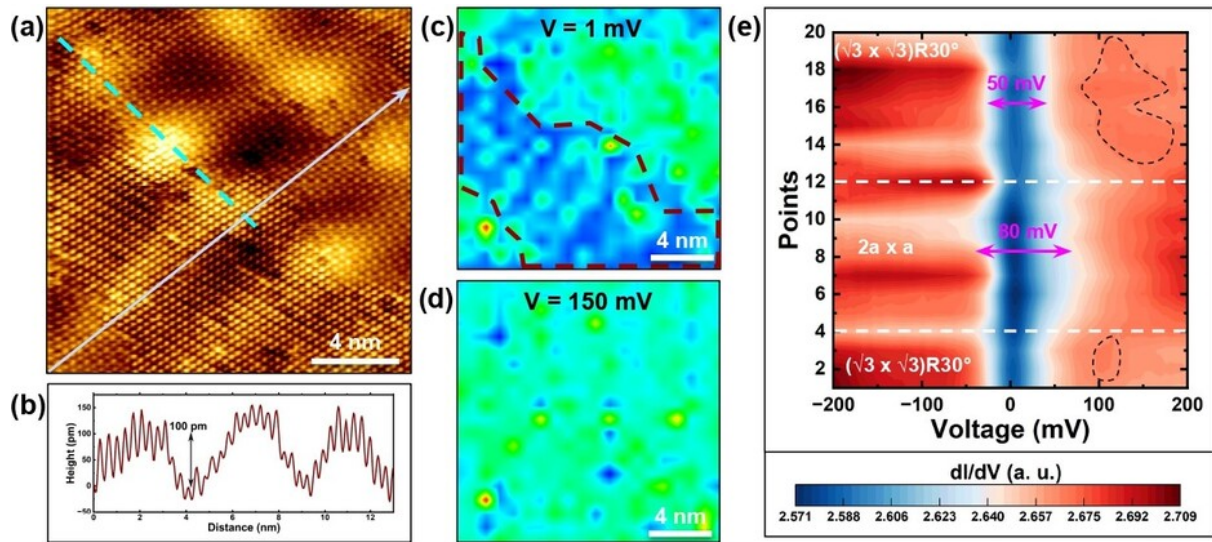


Figure 9.6 | STS of $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ and $2a_0 \times a_0$ modulated region. (a) The same STM image is shown as in Figure 9.3 (a). (b) The height profile of interlayer Fe-intercalation with the corresponding line scan is shown by a dotted cyan line in the image (a). (c) LDOS map ($V = 250$ mV, $I = 0.7$ nA) taken on the region shown in the image (a) at a bias of 1 mV with red dotted region highlighting $2a_0 \times a_0$ modulated region. (d) LDOS map ($V = 250$ mV, $I = 0.7$ nA) taken on the region shown in the image (a) at a bias of 150 mV. (e) Color contour map of line spectra taken on the region in the image (a) as shown by a white line. The black dotted region shows peaks and the white dotted line shows region boundaries.

To study the two types of modulations in detail, a spectroscopic line scan was performed. Figure 9.6 (e) shows a color contour map of the dI/dV spectra taken along the line shown by the white line in Figure 9.6 (a). The gap in the $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulated region is found to be in the range of 50-60 mV whereas the gap in the $2a_0 \times a_0$ modulated region is around 80 mV which shows the weakening of the strength of the modulation in the $2a_0 \times a_0$ region. At positive bias, there is a broad peak observed in the $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulated region at around 100 mV which is attributed to the Kondo effect. Such peaks are absent in the $2a_0 \times a_0$ modulated region which shows a linear behaviour indicating no contribution from the Kondo effect.

Fe intercalation in FGT can lead to strong electronic correlations where intralayer intercalation can drive structural reconstructions in FGT. This modulation can be brought in FGT samples with variable concentrations from pristine to Fe_5GeTe_2 . Such type of modulations has not been observed in STM reports on Fe_4GeTe_2 and Fe_3GeTe_2 [85]. Further, the modulation can be brought about by Fe intercalation in the vdW gaps and also introduce new types of charge ordering such as $2a_0 \times a_0$ which has not been observed in any FGT systems before.

Chapter 10

Summary and Outlook

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10.1 Summary of the Work

Various types of vdW materials were studied such as zero band gap graphene, superconducting NbSe₂, semiconducting MnPS₃, insulating hBN and itinerant ferromagnetic metal Fe₃GeTe₂. Graphite and MnPS₃ were used as a starting material to work on followed by FGT which was thoroughly investigated using various techniques such as Scanning Tunneling Microscopy and Spectroscopy, Atomic Force Microscopy, Raman spectroscopy, High Resolution-Transmission Electron Microscopy and Transport measurements. Methods of exfoliation, optical contrast determination, AFM and Raman characterization along with photolithography and transfer techniques were optimized.

The exfoliation process was optimized using graphite as a conventional material and the acquired parameters were tested on other materials. Monolayer graphene was successfully exfoliated and characterized followed by the making of twisted bilayer graphene with a twist angle of 8.7°. The band gap of MnPS₃ was determined using transport measurements by employing its heterostructures and was calculated to be 2.75 eV.

Basic studies were carried out on FGT such as exfoliation with the successful isolation of a three-layer flake. Raman modes of FGT were studied and its dependence on the number of layers was investigated. Characteristic Raman peaks of FGT were observed at 120 cm⁻¹ and 154 cm⁻¹ whose intensity decreases as the thickness of exfoliated flakes increases. Fe concentration in FGT was characterized using HR-TEM measurements resulting in the stoichiometry of the sample being Fe_nGeTe₂ (3 ≤ n ≤ 5.25). Possible ways of Fe-intercalation were examined which are intralayer intercalation leading to structural change into Fe₄GeTe₂

and further to Fe_5GeTe_2 and interlayer intercalation leading to an increase in height and surface corrugation of the material.

The time evolution of oxidation of exfoliated FGT flakes was thoroughly studied using techniques such as Raman spectroscopy, AFM and transport measurements. Oxidized flakes show two prominent Raman peaks at 124 cm^{-1} and 142 cm^{-1} . It was found that the rate of oxidation increases exponentially with temperature. The evolution of surface roughness and thickness of exfoliated flakes were observed to increase in a sigmoidal fashion. Roughness was found to reach saturation after around 15-20 days after having initiated at around 8 hrs from exfoliation which was due to Fe-O and Te-O bond formation. The thickness of flakes reached saturation in around 10 days after having initiated in around a day from exfoliation to almost doubling at saturation which was due to interlayer oxygen intercalation. Interlayer oxidation of FGT was hypothesized considering the results obtained by exfoliating the samples on PDMS and was confirmed by transport measurements.

STM tips were prepared using tungsten tips by electrochemical etching method and the parameters were optimized to obtain sharp tips suitable for STM measurements. FGT bulk crystal was affixed on the sample plate and the surface was exfoliated to obtain atomically flat regions for measurements.

Pristine FGT was characterized by Scanning Tunneling Microscopy and Spectroscopy at 4.3 K. A detailed study on various types of vacancies namely, Te, Fe I, Fe II, and a combination of them was carried out. The contrast of Te vacancy was highest which was seen as depression on the surface with Fe I & II, Fe I and Fe II vacancies causing less contrast in the said sequence. Spectroscopic studies reveal increased LDOS as we go from pristine to Te vacancy. Kondo resonance peak broadens going from pristine to Te vacancy. A Moire pattern with a periodicity of $7.5a_0 \times 15a_0$ was observed which showed metallic characteristics distinct from the pristine sample.

Charge ordering were observed in Fe-intercalated FGT regions and were studied using STM and STS. $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulation was characterized in FGT with Fe-intercalation inside the layer leading to structural change and giving stoichiometry of the sample to be Fe_5GeTe_2 . A gap opening of 46 mV was calculated in the sample. Interplay of Pristine FGT with $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ ordering was studied in an intralayer Fe-intercalated region. The gap was seen to broaden with a calculated value of 76 mV and the LDOS was found to increase away from fermi energy in the modulated region. $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ and $2a_0 \times a_0$ ordering

were studied in an interlayer Fe-intercalated region. Spectral studies revealed a lower LDOS in $2a_0 \times a_0$ modulated region at fermi level with the band gap of $2a_0 \times a_0$ modulated region in a range of 80 mV as compared to 50 mV in $(\sqrt{3}a_0 \times \sqrt{3}a_0)R30^\circ$ modulated region. These studies reveal the formation of charge ordering in FGT can be achieved through Fe-intercalation either inside the layer or in between the layers.

10.2 New Advancements the Thesis has Made

Charge ordering have been thoroughly studied and the results introduce a novel class of materials namely the FGT family that possess strongly correlated electronic systems. Charge ordering was shown to be introduced by intercalating the pristine FGT sample with Fe atoms inside the layer. Also, a novel modulation was observed by Fe intercalation in the vdW gap. This study not only puts forward strong electronic correlations in Fe-intercalated FGT but also provides new perspectives for different types of intercalation in various materials to probe for Charge density waves.

Raman studies will provide an easy and non-destructive way to not only characterize pristine FGT flakes but to also check the level of degradation the FGT sample has attained. Clean and flat samples are very pivotal in heterostructure preparation, the surface roughness studies using AFM will be helpful in examining the quality of the flake before transfer. Together Raman spectroscopic and AFM studies will give concluding evidence of the quality of FGT flakes. This study can be further applied to other oxidizing or degrading materials to characterize them.

Finally, unconventional superconductivity in FGT is being proposed considering factors such as an antiferromagnetic state that can be achieved through oxidation or Co doping, Charge ordering that are shown to be formed by Fe-intercalation and also varying electrical properties with controlled time-dependent oxidation. All these factors along with the quasi-2D nature of FGT makes it a classic candidate for exploring the holy grail of technology which is high-temperature superconductivity.

The work presented in this thesis is a part of two upcoming publications under preparation which are as follows:

- [1] **Atomic scale fingerprints of excess Fe in Fe_3GeTe_2 .**
- [2] **Surface and interlayer oxidation induced changes in vdW ferromagnet Fe_3GeTe_2 .**

10.3 Future Studies Intended

Homostructures with a twist angle show properties that are wildly different not only from the parent compound but also from the same system with a slightly different twist angle. So, the twisted bilayer graphene obtained with a twist angle of 8.7° will be probed using STM for the observation of Moiré patterns along with transport measurements.

The oxidation of FGT flakes have already been studied in detail. Now, the focus will be on probing exfoliated Fe-intercalated flakes with controlled oxidation to check for correlations between the amount of Fe atoms and the rate of oxidation as Fe is the main factor in the oxidation of FGT. The work will be carried out by the techniques used for FGT oxidation which are Raman spectroscopy, AFM and transport measurements along with cross-sectional TEM.

Heterostructures of ferromagnetic FGT and superconducting NbSe₂ will be prepared to check for the interplay between magnetism and superconductivity in the 2D limit. Since the prospects of FGT being a superconductor are high, the proximity-induced superconductivity from NbSe₂ to FGT will be the main focus of the study.

Appendix A

Transport Measurement Setup

Lithography using STM Tip

STM tips were used to make micron-sized patterns on sputter-deposited gold by taking advantage of the sharpness of the tips. The STM tips were coupled to a transfer stage and the substrate was positioned under the microscope in a manner similar to the flake transfer system and the desired pattern was etched using the fine motions of the XYZ transfer stage. A typical lithography pattern is shown in [Figure A.1 \(a\)](#).

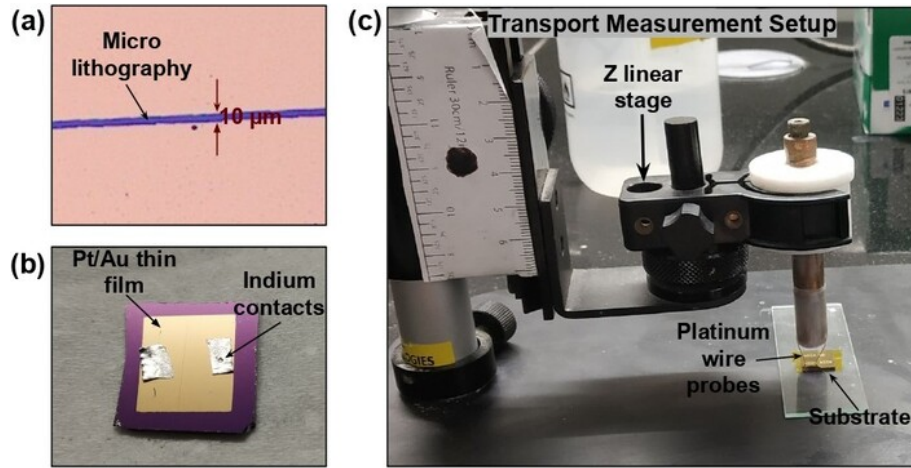


Figure A.1 | Transport Measurement Setup. (a) Microlithography pattern of 10 μm using STM tip. (b) Indium foil as intermediary contact between sputter-deposited gold and platinum probes. (c) Transport measurement setup.

Indium Foil as Contacts

Indium foil has been shown to make very good interfacial contacts with gold by cold welding method [31]. So 0.1 mm thick indium foil was used as an intermediary between the sputter-deposited gold and platinum wire contacts as shown in [Figure A.1 \(b\)](#).

The Measurement Setup

Two platinum wires of 0.25 mm thickness were used as probes which were coupled to the z-translational stage. The platinum probes were brought in contact with the indium foil and the whole assembly was stabilized for transport measurements as shown in [Figure A.1 \(c\)](#).

Appendix B

Lock-in Amplifier Technique

Lock-in Amplifier Working

Lock-in amplifiers are used to extract signals that are comparable to or even smaller than noise. A reference signal (modulation voltage) is supplied into the lock-in which has the same frequency and phase as the expected signal. Both these signals are multiplied and integrated over time, which gives a positive value to the expected signal and the noise is reduced to zero. A low pass filter then picks up the signal by averaging the output after the integration using some fixed parameter (time constant and sensitivity).

STS Data Acquisition

Since extracting the dI/dV - V curve is extremely noisy [86], an SR-830 Lock-in amplifier was used with a time constant, sensitivity, and modulation voltage being 100 ms, 500 mV, and 6 mV respectively.

A sinusoidal voltage was used as a reference voltage and the resulting voltage becomes,

$$V = V_{bias} + V_{mod} \sin \omega t$$

As the current is a function of the bias voltage, the modulated current also follows a sinusoidal relationship and is given as,

$$I_{tunneling} = I(V) = I(V_{bias} + V_{mod} \sin \omega t)$$

and its Taylor expansion is,

$$I_{tunneling} = I(V_{bias}) + \frac{dI(V_{bias})}{dV} V_{mod} \sin \omega t + \frac{d^2 I(V_{bias})}{dV^2} V_{mod}^2 \sin^2 \omega t + \dots$$

where the coefficient of the second term is proportional to the DOS of the sample, and the coefficient of the third term measures the vibrational energy levels. Thus, dI/dV - V curve is extracted by using the lock-in amplifier.

Bibliography

- [1] Flicker, F. (2023, April 27). ‘Why we must inspire people with the magic of condensed matter physics’. *New Scientist*.
- [2] Kaxiras, E., & Joannopoulos, J. D. (2019). ‘*Quantum Theory of Materials*’. Cambridge University Press.
- [3] Peierls, R. (1930). ‘Zur Theorie der elektrischen und thermischen Leitfähigkeit von Metallen’. *Annalen Der Physik*, 396(2), 121–148.
- [4] Peierls, R., & Roberts, L. D. (1956). ‘*Quantum Theory of Solids*’. *Physics Today*, 9(5), 29.
- [5] Zhu, X., Guo, J., Zhang, J., & Plummer, E. W. (2017). ‘Misconceptions associated with the origin of charge density waves’. *Advances in Physics: X*, 2(3), 622–640.
- [6] Chen, C., Choe, J., & Morosan, E. (2016). ‘Charge density waves in strongly correlated electron systems’. *Reports on Progress in Physics*, 79(8), 084505.
- [7] Onnes, H.K. (1911). ‘The Superconductivity of Mercury’. *Comm. Phys. Lab. Univ., Leiden*, 122-124.
- [8] Bardeen, J., Cooper, L. N., & Schrieffer, J. R. (1957). ‘Theory of superconductivity’. *Physical Review*, 108(5), 1175–1204.
- [9] Kautz, R. L. (2012). ‘*100 Years of Superconductivity*’. Edited by Horst Rogalla and Peter H. Kes. CRC Press.
- [10] Kamihara, Y., Hiramatsu, H., Hirano, M., Kawamura, R., Yanagi, H., Kamiya, T., & Hosono, H. (2006). Iron-Based Layered Superconductor: LAOFEP. *Journal of the American Chemical Society*, 128(31), 10012–10013.
- [11] Paras, Yadav, K., Kumar, P., Teja, D. R., Chakraborty, S., Chakraborty, M., Mohapatra, S., Sahoo, A., Chou, M. M. C., Liang, C., & Hang, D. (2022). ‘A review on Low-Dimensional Nanomaterials: Nanofabrication, Characterization and Applications’. *Nanomaterials*, 13(1), 160.
- [12] Wang, Q. H., Kalantar-zadeh, K., Kis, A., Coleman, J. N., & Strano, M. S. (2012). ‘Electronics and optoelectronics of two-dimensional transition metal dichalcogenides’. *Nature Nanotechnology*, 7(11), 699–712.
- [13] Burch, K. S., Mandrus, D., & Park, J. (2018). ‘Magnetism in two-dimensional van der Waals materials’. *Nature*, 563(7729), 47–52.
- [14] Lin, G., Li, M., Fan, Q., Liang, K., Hu, B., & Huang, Q. (2023). ‘Intercalation of Metal into Transition Metal Dichalcogenides in Molten Salts’. *Small*.

- [15] Rajapakse, M., Karki, B., Abu, U. O., Pishgar, S., Musa, R. K., Riyadh, S. M. S., Yu, M., Суманасекепа, Г., & Jasiński, J. B. (2021). ‘Intercalation as a versatile tool for fabrication, property tuning, and phase transitions in 2D materials’. *Npj 2D Materials and Applications*, 5(1).
- [16] Lei, Y., Zhang, T., Lin, Y., Granzier-Nakajima, T., Bepete, G., Kowalczyk, D. A., Lin, Z., Zhou, D. L., Schranghamer, T. F., Dodda, A., Sebastian, A., Chen, Y., Liu, Y., Pourtois, G., Kempa, T. J., Schuler, B., Edmonds, M. T., Quek, S. Y., Wurstbauer, U., . . . Terrones, M. (2022). ‘Graphene and Beyond: Recent Advances in Two-Dimensional Materials Synthesis, Properties, and Devices’. *ACS Nanoscience Au*, 2(6), 450–485.
- [17] Huang, B., Clark, G., Navarro-Moratalla, E., Klein, D. R., Cheng, R., Seyler, K. L., Zhong, D., Schmidgall, E. R., McGuire, M. A., Cobden, D., Wang, Y., Xiao, D., Jarillo-Herrero, P., & Xu, X. (2017). ‘Layer-dependent ferromagnetism in a van der Waals crystal down to the monolayer limit’. *Nature*, 546(7657), 270–273.
- [18] Gong, C., Li, L., Li, Z., Ji, H., Stern, A. C., Xia, Y., Cao, T., Bao, W., Wang, C., Wang, Y., Qiu, Z. Q., Cava, R. J., Louie, S. G., Xia, J., & Zhang, X. (2017). ‘Discovery of intrinsic ferromagnetism in two-dimensional van der Waals crystals’. *Nature*, 546(7657), 265–269.
- [19] Deiseroth, H. J., Aleksandrov, K., Reiner, C., Kienle, L., & Kremer, R. K. (2006). ‘Fe₃GeTe₂ and Ni₃GeTe₂ – Two New Layered Transition-Metal Compounds: Crystal Structures, HRTEM Investigations, and Magnetic and Electrical Properties’. *European Journal of Inorganic Chemistry*, 2006(8), 1561–1567.
- [20] Liu, Q., Xing, J., Zhou, J., Guo, Y., Jiang, X., Qi, Y., & Zhao, J. (2022). ‘Layer-dependent magnetic phase diagram in Fe_nGeTe₂ (3 ≤ n ≤ 7) ultrathin films’. *Communications Physics*, 5(1).
- [21] Jiang, S., Shan, J., & Mak, K. F. (2018). ‘Electric-field switching of two-dimensional van der Waals magnets’. *Nature Materials*, 17(5), 406–410.
- [22] Li, Y., Hu, X., Fereidouni, A., Basnet, R., Pandey, K. C., Wen, J., Liu, Y., Zheng, H., Churchill, H., Hu, J., Petford-Long, A. K., & Phatak, C. (2023). ‘Visualizing the Effect of Oxidation on Magnetic Domain Behavior of Nanoscale Fe₃GeTe₂ for Applications in Spintronics’. *ACS Applied Nano Materials*, 6(6), 4390–4397.
- [23] Zhuang, H., Kent, P., & Hennig, R. G. (2016). ‘Strong anisotropy and magnetostriction in the two-dimensional Stoner ferromagnet Fe₃GeTe₂’. *Physical Review*, 93(13).
- [24] Yang, H., Bansal, N., Rüßmann, P., Hoffmann, M., Zhang, L., Go, D., Li, Q., Haghighirad, A., Sen, K., Blügel, S., Tacon, M. L., Mokrousov, Y., & Wulfschkel, W.

- (2022). ‘Magnetic domain walls of the van der Waals material Fe_3GeTe_2 ’. *2D Materials*, 9(2), 025022.
- [25] Li, G., Ma, S., Li, Z., Zhang, Y., Diao, J., Xia, L., Zhang, Z., & Huang, Y. (2022). ‘High-Quality Ferromagnet Fe_3GeTe_2 for High-Efficiency Electromagnetic Wave Absorption and Shielding with Wideband Radar Cross Section Reduction’. *ACS Nano*, 16(5), 7861–7879.
- [26] Zhang, K., Han, S., Lee, Y., Coak, M. J., Kim, J., Hwang, I., Son, S., Shin, J., Lim, M., Jo, D., Kim, K., Kim, D., Lee, H., & Park, J. (2020). ‘Gigantic Current Control of Coercive Field and Magnetic Memory Based on Nanometer-Thin Ferromagnetic van der Waals Fe_3GeTe_2 ’. *Advanced Materials*, 33(4).
- [27] Fei, Z., Huang, B., Malinowski, P., Wang, W., Song, T., Sanchez, J. J., Wang, Y., Xiao, D., Zhu, X., May, A. F., Wu, W., Cobden, D., Chu, J., & Xu, X. (2018). ‘Two-dimensional itinerant ferromagnetism in atomically thin Fe_3GeTe_2 ’. *Nature Materials*, 17(9), 778–782.
- [28] Roemer, R., Liu, C., & Zou, K. (2020). ‘Robust ferromagnetism in wafer-scale monolayer and multilayer Fe_3GeTe_2 ’. *Npj 2D Materials and Applications*, 4(1).
- [29] Hu, X., Zhao, Y., Shen, X., Krasheninnikov, A. V., Chen, Z., & Sun, L. (2020). ‘Enhanced Ferromagnetism and Tunable Magnetism in Fe_3GeTe_2 Monolayer by Strain Engineering’. *ACS Applied Materials & Interfaces*, 12(23), 26367–26373.
- [30] Deng, Y., Yu, Y., Song, Y., Zhang, J., Wang, N., Sun, Z., Yi, Y., Wu, Y., Wu, S., Zhu, J., Wang, J., Chen, X. H., & Zhang, Y. (2018). ‘Gate-tunable room-temperature ferromagnetism in two-dimensional Fe_3GeTe_2 ’. *Nature*, 563(7729), 94–99.
- [31] Albarakati, S., Tan, C., Chen, Z., Partridge, J. G., Zheng, G., Farrar, L., Mayes, E., Field, M. R., Lee, C., Wang, Y., Xiong, Y., Tian, M., Xiang, F., Hamilton, A. R., Tretiakov, O. A., Culcer, D., Zhao, Y., & Wang, L. (2019). ‘Antisymmetric magnetoresistance in van der Waals Fe_3GeTe_2 /graphite/ Fe_3GeTe_2 trilayer heterostructures’. *Science Advances*, 5(7).
- [32] Zhou, L., Huang, J., Tang, M., Qiu, C., Qin, F., Zhang, C., Li, Z., Wu, D., & Yuan, H. Q. (2022). ‘Gate-tunable spin valve effect in Fe_3GeTe_2 -based van der Waals heterostructures’. *InfoMat*, 5(3).
- [33] Wang, X., Tang, J., Xia, X., He, C., Zhang, J., Liu, Y., Wan, C., Fang, C., Guo, C., Yang, W., Yuan, G., Zhang, X., Xu, H., Wei, J., Liao, M., Lu, X., Feng, J., Li, X., Peng, Y., . . . Han, X. (2019). ‘Current-driven magnetization switching in a van der Waals ferromagnet Fe_3GeTe_2 ’. *Science Advances*, 5(8).
- [34] Chyczewski, S. T., Shi, J., Lee, H., Furlanetto, P. F., Xu, K., Van Der Zande, A. M., & Zhu, W. (2023). ‘Probing Antiferromagnetism in Exfoliated Fe_3GeTe_2 using Magneto-transport Measurements’. *Nanoscale*, 15(34), 14061–14067.

- [35] Yi, J. (2015). ‘Novel physical properties of non-trivial magnetic materials: $\text{CrI}_3/\text{NbS}_2$, MnSi and Fe_3GeTe_2 ’. *PhD diss., University of Tennessee*.
- [36] Kim, D., Park, S., Lee, S. Y., Yoon, J. W., Joo, S., Kim, T., Min, K., Park, S., Kim, C., Moon, K., Lee, C., Hong, J., & Hwang, C. (2019). Antiferromagnetic coupling of van der Waals ferromagnetic Fe_3GeTe_2 . *Nanotechnology*, 30(24), 245701.
- [37] Novoselov, K. S., Geim, A. K., Morozov, S. v, Jiang, D., Zhang, Y., Dubonos, S. v, Grigorieva, I. v, & Firsov, A. A. (2004). ‘Electric field effect in atomically thin carbon films’. *Science*, 306(5696), 666–669.
- [38] Klapwijk, T. M. (2004). ‘Proximity effect from an Andreev perspective’. *Journal of Superconductivity*, 17(5), 593–611.
- [39] Goossens, D., Wildes, A., Ritter, C., & Hicks, T. J. (2000). ‘Ordering and the nature of the spin flop phase transition in MnPS_3 ’. *Journal of Physics: Condensed Matter*, 12(8), 1845–1854.
- [40] Molaei, M. J., Younas, M., & Reza kazemi, M. (2021). ‘A comprehensive review on recent advances in Two-Dimensional (2D) Hexagonal Boron Nitride’. *ACS Applied Electronic Materials*, 3(12), 5165–5187.
- [41] Chen, T., Mastropaolo, E., Bunting, A., Stevenson, T. J., & Cheung, R. (2012). ‘Optimization of the visibility of graphene on poly-Si film by thin-film optics engineering’. *Journal of Vacuum Science and Technology*, 30(6).
- [42] Sun, Y., Pang, S., & Zhang, J. (2021). ‘Review of Raman spectroscopy of two-dimensional magnetic van der Waals materials’. *Chinese Physics B*, 30(11), 117104.
- [43] Sutikno, S., Susilo, S., & Raharja, H. D. (2018b). ‘Photoresist: fabrication, characterization and its sensitivity on the exposures of X-Ray and ultraviolet’. *IOP Conference Series*, 367, 012022.
- [44] Castellanos-Gómez, A., Buscema, M., Molenaar, R., Singh, V., Janssen, L., Van Der Zant, H. S. J., & Steele, G. A. (2014). ‘Deterministic transfer of two-dimensional materials by all-dry viscoelastic stamping’. *2D Materials*, 1(1), 011002.
- [45] Wakafuji, Y., Onodera, M., Masubuchi, S., Moriya, R., Zhang, Y., Watanabe, K., Taniguchi, T., & Machida, T. (2022). ‘Evaluation of polyvinyl chloride adhesion to 2D crystal flakes’. *Npj 2D Materials and Applications*, 6(1).
- [46] Shearer, C. J., Slattery, A. D., Stapleton, A. J., Shapter, J. G., & Gibson, C. T. (2016). ‘Accurate thickness measurement of graphene’. *Nanotechnology*, 27(12), 125704.

- [47] Malard, L. M., Pimenta, M. A., Dresselhaus, G., & Dresselhaus, M. S. (2009). 'Raman spectroscopy in graphene'. *Physics Reports*, 473(5–6), 51–87.
- [48] Daniel R. Cooper, Benjamin D'Anjou, Nageswara Ghattamaneni, Benjamin Harack, Michael Hilke, Alexandre Horth, Norberto Majlis, Mathieu Massicotte, Leron Vandsburger, Eric Whiteway, Victor Yu. (2012). 'Experimental Review of Graphene'. *International Scholarly Research Notices*, vol. 2012, Article ID 501686.
- [49] Cao, Y., Fatemi, V., Fang, S., Watanabe, K., Taniguchi, T., Kaxiras, E., & Jarillo-Herrero, P. (2018). 'Unconventional superconductivity in magic-angle graphene superlattices'. *Nature*, 556(7699), 43–50.
- [50] Hou, Y., Ren, X., Fan, J., Wang, G., Dai, Z., Jin, C., Wang, W., Zhu, Y., Zhang, S., Liu, L., & Zhong, Z. (2020). 'Preparation of twisted bilayer graphene via the wetting transfer method'. *ACS Applied Materials & Interfaces*, 12(36), 40958–40967.
- [51] Jório, A., & Cançado, L. G. (2013). 'Raman spectroscopy of twisted bilayer graphene'. *Solid State Communications*, 175–176, 3–12.
- [52] Nirmalraj, P. N., Lutz, T., Kumar, S., Duesberg, G. S., & Boland, J. J. (2010). 'Nanoscale mapping of electrical resistivity and connectivity in graphene strips and networks'. *Nano Letters*, 11(1), 16–22.
- [53] Kurosawa, Ko, Saito, Shozo, & Yamaguchi, Yasuo. (1983). 'Neutron diffraction study on MnPS₃ and FePS₃'. *Journal of the Physical Society of Japan*, 52(11), 3919–3926.
- [54] Harms, N. C., Kim, H. S., Clune, A., Smith, K. B., O'Neal, K., Haglund, A., Mandrus, D., Liu, Z., Haule, K., Vanderbilt, D., & Musfeldt, J. L. (2020). 'Piezochromism in the magnetic chalcogenide MnPS₃'. *Npj Quantum Materials*, 5(1).
- [55] Kong, X., Berlijn, T., & Liang, L. (2021). 'Thickness and Spin Dependence of Raman Modes in Magnetic Layered Fe₃GeTe₂'. *Advanced Electronic Materials*, 7(7).
- [56] Du, L., Tang, J., Zhao, Y., Li, X., Yang, R., Hu, X., Bai, X., Wang, X., Watanabe, K., Taniguchi, T., Shi, D., Yu, G., Bai, X., Hasan, T., Zhang, G., & Sun, Z. (2019). 'Lattice Dynamics, Phonon Chirality, and Spin-Phonon Coupling in 2D Itinerant Ferromagnet Fe₃GeTe₂'. *Advanced Functional Materials*, 29(48), 1904734.
- [57] Van Velson, N., Zobeiri, H., & Wang, X. (2023). 'Thickness-Dependent Raman Scattering from Thin-Film Systems'. *Journal of Physical Chemistry C*, 127(6), 2995–3004.

- [58] Wu Y, Hu Y, Wang C, et al. (2023). ‘Large enhancement of Curie temperature in Fe_3GeTe_2 by Fe intercalation in the van der Waals gap’. *Research Square*.
- [59] Iturriaga, H., Martinez, L. M., Mai, T., Biacchi, A. J., Augustin, M., Walker, A. R. H., Sanad, M. F., Sreeprasad, T. S., Liu, Y., Santos, E. J. G., Petrović, C., & Singamaneni, S. R. (2023). ‘Magnetic properties of intercalated quasi-2D $\text{Fe}_{3-x}\text{GeTe}_2$ van der Waals magnet’. *Npj 2D Materials and Applications*, 7(1).
- [60] Wang, G., Pandey, R., & Karna, S. P. (2016). ‘Physics and chemistry of oxidation of two-dimensional nanomaterials by molecular oxygen’. *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 7(1).
- [61] Purbawati, A., Coraux, J., Vogel, J., Hadj-Azzem, A., Wu, N., Bendiab, N., Jegouso, D., Renard, J., Marty, L., Bouchiat, V., Sulpice, A., Aballe, L., Foerster, M., Genuzio, F., Locatelli, A., Mentes, T. O., Han, Z., Sun, X., Núñez-Regueiro, M., & Rougemaille, N. (2020). ‘In-Plane Magnetic Domains and Néel-like Domain Walls in Thin Flakes of the Room Temperature CrTe_2 Van der Waals Ferromagnet’. *ACS Applied Materials & Interfaces*, 12(27), 30702–30710.
- [62] Chang, Y., Nishimura, T., & Nagashio, K. (2021). ‘Thermodynamic perspective on the oxidation of layered materials and surface oxide amelioration in 2D devices’. *ACS Applied Materials & Interfaces*, 13(36), 43282–43289.
- [63] Gweon, H. K., Lee, S. Y., Kwon, H. Y., Jeong, J., Chang, H. J., Kim, K., Qiu, Z. Q., Ryu, H., Jang, C., & Choi, J. W. (2021). ‘Exchange Bias in Weakly Interlayer-Coupled van der Waals Magnet Fe_3GeTe_2 ’. *Nano Letters*, 21(4), 1672–1678.
- [64] Kim, D. S., Kee, J. Y., Lee, J., Liu, Y., Kim, Y., Kim, N., Hwang, C., Kim, W., Petrović, C., Lee, D. R., Jang, C., Ryu, H., & Choi, J. W. (2021). ‘Surface oxidation in a van der Waals ferromagnet $\text{Fe}_{3-x}\text{GeTe}_2$ ’. *Current Applied Physics*, 30, 40–45.
- [65] Arrhenius, S. (1889). ‘Über die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Säuren’. *Zeitschrift Für Physikalische Chemie*, 4U(1), 226–248.
- [66] Perez, J. (2015). Computational Chemistry: ‘A Practical guide for applying techniques to Real-World problems’. www.academia.edu.
- [67] Purdie, D. G., Pugno, N., Taniguchi, T., Watanabe, K., Ferrari, A. C., & Lombardo, A. (2018). ‘Cleaning interfaces in layered materials heterostructures’. *Nature Communications*, 9(1).
- [68] Zhao, Q., Xia, C., Zhang, H., Jiang, B., Xie, T., Lou, K., & Bi, C. (2023). ‘Ferromagnetism of Nanometer Thick Sputtered Fe_3GeTe_2 Films in the Absence of Two-Dimensional Crystalline Order: Implications for Spintronics Applications’. *ACS Applied Nano Materials*, 6(4), 2873–2882.

- [69] Sing, K. S. W., & Williams, R. T. (2004). 'The use of molecular probes for the characterization of nanoporous adsorbents'. *Particle & Particle Systems Characterization*, 21(2), 71–79.
- [70] Wang, S., Xue, J., Xu, D., He, J., Dai, Y., Xia, T., Huang, Y., He, Q., Duan, X., & Lin, Z. (2023). 'Electrochemical molecular intercalation and exfoliation of solution-processable two-dimensional crystals'. *Nature Protocols*, 18(9), 2814–2837.
- [71] Park, T. E., Peng, L., Liang, J., Hallal, A., Yasin, F., Zhang, X., Song, K., Kim, S. J., Kim, K., Weigand, M., Schütz, G., Finizio, S., Raabe, J., Garcia, K., Xia, J., Zhou, Y., Ezawa, M., Liu, X., Chang, J., . . . Woo, S. H. (2021). 'Néel-type skyrmions and their current-induced motion in van der Waals ferromagnet-based heterostructures'. *Physical Review*, 103(10).
- [72] Tu, Z., Xie, T., Lee, Y., Zhou, J., Admasu, A. S., Gong, Y., Valanoor, N., Cumings, J., Cheong, S., Takeuchi, I., Cho, K., & Gong, C. (2021). 'Ambient effect on the Curie temperatures and magnetic domains in metallic two-dimensional magnets'. *Npj 2D Materials and Applications*, 5(1).
- [73] Binnig, G., & Rohrer, H. (1987). 'Scanning tunneling microscopy—from birth to adolescence'. *Reviews of Modern Physics*, 59(3), 615–625.
- [74] Binnig, G., & Rohrer, H. (1983). 'Scanning tunneling microscopy'. *Surface Science*, 126(1–3), 236–244.
- [75] Prasad, R., & Singh, D. K. (2020). 'Low cost electrical probe station using etched tungsten nanoprobe: role of cathode geometry'. *Nano Express*, 1(2), 020042.
- [76] Zhang, Y., Lu, H., Zhu, X., Tan, S., Feng, W., Liu, Q., Zhang, W., Chen, Q., Liu, Y., Luo, X., Xie, D., Luo, L., Zhang, Z., & Lai, X. (2018). 'Emergence of Kondo lattice behavior in a van der Waals itinerant ferromagnet, Fe₃GeTe₂'. *Science Advances*, 4(1).
- [77] Trainer, C., Armitage, O. R., Lane, H., Rhodes, L. C., Chan, E., Benedičić, I., Rodríguez-Rivera, J. A., Fabelo, Ó., Stock, C., & Wahl, P. (2022). 'Relating spin-polarized STM imaging and inelastic neutron scattering in the van der Waals ferromagnet Fe₃GeTe₂'. *Physical Review*, 106(8).
- [78] Carnevali, V., Marcantoni, S., & Peressi, M. (2021). 'Moiré patterns generated by stacked 2D lattices: A general algorithm to identify primitive coincidence cells'. *Computational Materials Science*, 196, 110516.
- [79] Reshak, A. (2009). 'Copper-Intercalated TiS₂: Electrode Materials for Rechargeable Batteries as Future Power Resources'. *Journal of Physical Chemistry A*, 113(8), 1635–1645.

- [80] Rana, D., Bhakar, M., Basavaraja, G., Bera, S., Saini, N. L., Pradhan, S. K., Mondal, M., Kabir, M., & Sheet, G. (2023). ‘High transport spin polarization in the van der Waals ferromagnet Fe_4GeTe_2 ’. *Physical Review*, 107(22).
- [81] Wu, X., Lei, L., Yin, Q., Zhao, N., Li, M., Wang, Z., Liu, Q., Song, W., Ma, H., Ding, P., Cheng, Z., Li, K., Lei, H., & Wang, S. (2021). ‘Direct observation of competition between charge order and itinerant ferromagnetism in the van der Waals crystal $\text{Fe}_{5-x}\text{GeTe}_2$ ’. *Physical Review*, 104(16).
- [82] Ershadrad, S., Ghosh, S., Wang, D., Kvashnin, Y., & Sanyal, B. (2022). ‘Unusual Magnetic Features in Two-Dimensional Fe_5GeTe_2 Induced by Structural Reconstructions’. *Journal of Physical Chemistry Letters*, 13(22), 4877–4883.
- [83] Ly, T. T., Park, J., Kim, K., Ahn, H., Lee, N. J., Kim, K., Park, T., Duvjir, G., Lam, N. H., Jang, K., You, C., Jo, Y., Kim, S., Lee, C., Kim, S., & Kim, J. (2021). ‘Direct Observation of Fe-Ge Ordering in $\text{Fe}_{5-x}\text{GeTe}_2$ Crystals and Resultant Helimagnetism’. *Advanced Functional Materials*, 31(17).
- [84] Laipan, M., Xiang, L., Yu, J., Martin, B., Zhu, R. S., Zhu, J., He, H., Clearfield, A., & Sun, L. (2020). ‘Layered intercalation compounds: Mechanisms, new methodologies, and advanced applications’. *Progress in Materials Science*, 109, 100631.
- [85] May, A. F., Ovchinnikov, D., Zheng, Q., Hermann, R. P., Calder, S., Huang, B., Fei, Z., Liu, Y., Xu, X., & McGuire, M. A. (2019). ‘Ferromagnetism Near Room Temperature in the Cleavable van der Waals Crystal Fe_5GeTe_2 ’. *ACS Nano*, 13(4), 4436–4442.
- [86] Rejaul, S. k. (2018). ‘Exploring Molecule-Metal and Molecule-Topological Insulator Interface at Atomic Scale’. *PhD diss., Indian Institute of Science Education and Research, Pune*.