

Synthesis and Characterization of 2D Tellurene Flakes for Device Application

A Thesis

submitted to

Indian Institute of Science Education and Research Pune

in partial fulfillment of the requirements for the

BS-MS Dual Degree Programme

by

Rohan Thangaraj



Indian Institute of Science Education and Research Pune

Dr. Homi Bhabha Road,
Pashan, Pune 411008, INDIA.

April, 2024

Supervisor: Dr. Atikur Rahman

© Rohan Thangaraj 2024

All rights reserved

Certificate

This is to certify that this dissertation entitled “Synthesis and Characterization of 2D Tellurene Flakes for Device Application” towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents study/work carried out by Rohan Thangaraj at Indian Institute of Science Education and Research under the supervision of Dr. Atikur Rahman, Associate Professor, Department of Physics, during the academic year 2023-2024.



Dr. Atikur Rahman

Committee:

Dr. Atikur Rahman

Dr. Aparna Deshpande

This thesis is dedicated to:
My parents (Dr. R Thangaraj and Mrs. S Kalaiselvi)

Declaration

I hereby declare that the matter embodied in the report entitled “Synthesis and Characterization of 2D Tellurene Flakes for Device Application” are the results of the work carried out by me at the Department of Physics, Indian Institute of Science Education and Research (IISER) Pune, under the supervision of Dr. Atikur Rahman, and the same has not been submitted elsewhere for any other degree. Wherever others contribute, every effort is made to indicate this clearly, with due reference to the literature and acknowledgement of collaborative research and discussions.



Rohan Thangaraj

20191154

Acknowledgments

I am deeply grateful to my supervisor, Dr. Atikur Rahman, for his unwavering support, invaluable guidance, and mentorship throughout my academic journey. His expertise, encouragement, and dedication to excellence have played a pivotal role in shaping my research endeavors and fostering my academic growth. I consider myself incredibly fortunate to have been mentored by someone of his caliber. Despite his busy schedule, he always made himself available for discussions, providing valuable insights and feedback. I am particularly thankful for the freedom he granted me throughout this project. Beyond academic matters, his guidance on personal and professional development has been invaluable to me. He has set a high standard for mentorship, and I am grateful for the opportunity to have worked under his guidance. As I embark on future endeavors, I can only hope to find (or become in far future) a supervisor as exceptional as him.

I am indebted to Dr. Aparna Deshpande, my Thesis Advisory Committee (TAC) member, for her insightful feedback, constructive criticism, and scholarly inputs that have enriched the quality of my work. She has shown high interest in my work. Despite her busy schedule, she made time for monthly meetings and gave constant inputs.

I extend my sincere thanks to my esteemed lab members, Mr. Avinash Mahapatra, Mr. Pawan Kumar, Mr. Sudipta Majumdar, Dr. Gokul M A, Ms. Manisha Rajput, Ms. Meghasree Basu and others for their friendly environment, discussions, collaborative efforts. This work wouldn't have been possible without these people and their support. I have to thank them for all the brainstorming sessions, for troubleshooting experiments, sharing insights, and clarifying all my doubts. I am sure to see them do ground breaking research in the future. Together, their contributions have not only advanced the progress of my research project but have also left a lasting impact on my personal and professional growth. I am truly grateful for the memorable moments shared in the lab, whether it be the laughter-filled celebrations of project milestones or the words of encouragement offered during moments of doubt.

I extend my heartfelt appreciation to my family, whose unwavering support has been the cornerstone of my academic journey. Specifically, I am deeply grateful to my father, Dr. R Thangaraj, whose wisdom, guidance, and unwavering belief in my potential have been a source of inspiration and strength. His encouragement to pursue my passions and overcome challenges has been invaluable, instilling in me the confidence to strive for excellence. Similarly, I am indebted to my mother, Mrs. S Kalaiselvi, for her boundless love, sacrifices, and unwavering support. Her nurturing presence and unwavering belief in my abilities have provided me with the reassurance and motivation needed to navigate the complexities of academic life. I also extend my gratitude to my sister, Mrs. Nanal Thangaraj, and my niece, Ms. M.N. Jivika, for their understanding, encouragement, and unwavering belief in my dreams. Their unwavering support and encouragement have been a source of comfort and motivation, reminding me of the importance of family bonds and shared aspirations.

Special thanks to Mr. Pranjali Panwar and Dr. Aparna Deshpande (once again!) for their collaboration on scanning tunneling microscopy (STM) and atomic force microscopy (AFM) measurements, which significantly enhanced the scope and depth of my research findings.

I am grateful to my dear friends for their unwavering support, encouragement throughout this academic journey.

I would like to acknowledge the support of my institute, IISER Pune, for providing state-of-the-art facilities, academic resources, and a conducive research environment that facilitated my academic pursuits.

I am grateful to the Department of Science and Technology (DST), Government of India, for their financial support through the INSPIRE fellowship, which enabled me to pursue my research aspirations and academic goals.

Special thanks are extended to the technical staff, including Mr. Nilesh Dumbre, Mr. Kartikeyan, Mr. Sudhir Lone and Mr. Anil Prathamshetti, for their assistance, cooperation, and logistical support throughout my tenure at the institute.

Lastly, I extend my gratitude to all individuals and entities who have contributed, directly or indirectly, to the successful completion of my master's thesis.

Thank you all! Thank you almighty!

Abstract

Tellurene, a single layer of tellurium atoms arranged in a zig-zag chain structure, is a recent addition to the family of 2D materials. It has a trigonal crystal lattice with inherent structural anisotropy. Tellurene has huge potential for nanoelectronic and opto-electronic applications. Tellurene has interesting properties e.g., semiconducting, photoconductive, thermoelectric, piezoelectric, topological, and acousto-optic properties making it suitable for application in electronics, sensors, optoelectronics and energy devices. Additionally, Tellurene exhibits extraordinary carrier mobility, high stretchability, and significant optical absorption.

Due to its inherent structural anisotropy, previously reported methods were not very successful in synthesizing 2D sheets. However, the solvothermal technique is a substrate-free solution process that can produce large area, high-quality Tellurene without the need for high growth temperature, delicate control of growth atmosphere, or specific substrate for growth, unlike other methods like CVD, PVD, etc. So far there hasn't been much in-depth study of electronic or optoelectronic properties of solution grown Tellurene. In this thesis we have synthesized 2D Tellurene using solvothermal technique and studied their properties in detail.

After synthesis, the morphology and structure of the samples were characterized by using SEM, TEM, XRD, AFM, STM and Raman spectroscopy. This work mainly involves the study of electrical and opto-electronic properties of Tellurene by fabricating devices using photo-lithography. The electrical properties such as mobility, on/off ratio, current density and opto-electronic properties such as rise time, fall time, on/off ratio were studied in detail. Devices with different contact material were made on the as-grown flakes. The contact resistance between various materials such as Platinum, Palladium, Nickel and Gold were studied. The effect of these contact materials on the properties of Tellurene flakes were also studied in detail. For the first time we herein report the observation of contact induced metallization of Tellurene flakes. The polarization dependent imaging of the samples were also performed.

Contents

Abstract	xi
List of Figures	xv
1 Introduction	1
1.1 2D materials	1
1.2 X-enes	2
1.3 Tellurene	3
2 Synthesis	5
2.1 Physical Vapor Deposition	5
2.2 Molecular Beam Epitaxy	6
2.3 Liquid Phase Exfoliation	6
2.4 Hydrothermal Synthesis	7
3 Structural Characterization	9
3.1 Optical Images	9
3.2 Scanning Electron Microscopy	10
3.3 Raman Spectroscopy	11
3.4 Atomic Force Microscopy	13
3.5 High Resolution Transmission Electron Microscopy	14
3.6 Energy Dispersive X-Ray Analysis	16
3.7 X-Ray Diffraction	17
3.8 X-ray Photoelectron Spectroscopy	18
3.9 Scanning Tunnelling Spectroscopy	19
4 Device Fabrication	21
4.1 2D Transfer	22
4.2 Photolithography	23
4.3 Metal Deposition	24
4.4 Liftoff	24
4.5 Fabrication Recipe	25

5	Electrical Characterization	27
5.1	Output Characteristics	28
5.2	Transfer Characteristics	30
5.3	Stability of Tellurene flakes	32
5.4	Contact resistance	34
5.5	Contact induced metallization	37
6	Optoelectronic Characterization	41
6.1	Photoresponse	41
6.2	Time resolved photocurrent	43
6.3	Spatially resolved photocurrent	45
6.4	Polarization dependence	46
7	Conclusion and future scope	49

List of Figures

1.1	Schematic of 2D van der Waals heterostructure as lego blocks [3]	2
1.2	Schematic of crystal structure of tellurene viewed from different directions [10]	3
2.1	Schematic of hypothesized growth process inside an autoclave from precursors to quantum dots to nanowires to 2D tellurene sheets	7
3.1	(a) Bright field optical images of as-grown tellurene flake under 100x magnification showcasing different structures (b) Dark field optical images of as-grown tellurene flake under 100x magnification (scale 20um for (a) and (b)	10
3.2	Scanning Electron Microscopic image of the as-grown tellurene flake showing different morphologies and smooth surfaces	11
3.3	(a) Raman spectra of the as-grown tellurene flakes. (b) schematic of various vibration modes corresponding to the raman peaks [7]	12
3.4	Raman mapping of as-grown tellurene flakes corresponding to their three major peaks depicting the intensity and peak position	13
3.5	Atomic force microscope image of a tellurene flake and its trace showing 36 nm of height	14
3.6	(a) HR-TEM image of an as-grown tellurene flake (b) IFFT of a selected area noise reduced FFT of the TEM image (c) SAED pattern of the as-grown flake	15
3.7	Graph depicting the interatomic separation in two direction	15
3.8	(a)EDX of the as-grown tellurene flakes obtained using HR-TEM (b)EDX of the as-grown tellurene flakes obtained using SEM	16
3.9	X-ray diffraction pattern of the synthesized tellurene flakes	17
3.10	X-ray photoelectron spectroscopy of the as-grown tellurene flake	18
3.11	(a) STM image of a tellurene flake (b) STS of a tellurene flake showing a bandgap of 0.39eV	19
4.1	Schematic of a dry transfer process	23
5.1	Graph showing the output characteristics of 2-probe tellurene device with chromium contact	28
5.2	Optical image of a fabricated 2-probe device on tellurene flake	29
5.3	Output characteristics of Pt, Pd and Ni contacted tellurene devices	29

5.4	(a) Optical image showing the graphene flake transferred onto a tellurene flake (b) Output characteristics of graphene contacted tellurene device	30
5.5	Output characteristics of gold contacted tellurene device	31
5.6	(a) Output characteristics of Pt contacted tellurene device with varying gate bias (b) Transfer characteristics of Pt contacted tellurene device (c) Linear fit of the I_{SD} vs V_{GS} curve to obtain mobility and V_{TH}	32
5.7	(a) I_{SD} vs V_{SD} of tellurene flakes in ambient and vacuum condition (b) I_{SD} vs V_{SD} of tellurene flakes before and after intense O_2 RIE treatment (c) I_{SD} vs V_{SD} of tellurene flakes before and after thermal annealing	33
5.8	(a) Schematic of transfer length geometry (b) Optical image of a transfer length pattern made on tellurene flake	34
5.9	I_{SD} vs V_{SD} characteristics for varying channel length and Total resistance vs channel length fit (TLM) for (a) Pt contact (b) Pd contact (c) Ni contact (d) current annealed Au contact	36
5.10	(a) I_{SD} vs V_{SD} characteristics for varying channel length in Au contacted TLM device before current annealing (b) I_{SD} vs V_{SD} characteristics for varying channel length in Au contacted TLM device after current annealing (c) Total resistance vs channel length fit (TLM) for Au contact	37
5.11	Graph of total resistance and I_{SD} as a function of temperature for Ni contacted tellurene device with $3\mu m$ channel length	38
5.12	Graph of total resistance and I_{SD} as a function of temperature for Pt contacted tellurene device with (a) $3\mu m$ channel length (b) $5\mu m$ channel length	39
5.13	Graph of total resistance and I_{SD} as a function of temperature for Pd contacted tellurene device with (a) $3\mu m$ channel length (b) $5\mu m$ channel length	39
6.1	(a) Photoresponse of tellurene flake with Pt contacts under illumination with 365nm wavelength LED (b) IV characteristics of tellurene under varying intensity of illumination	42
6.2	(a) Photocurrent as a function of power density of tellurene devices with Pt contacts under illumination with 365nm wavelength LED (b) Responsivity as a function of power density of tellurene devices with Pt contacts under illumination with 365nm wavelength LED	43
6.3	Photoresponse of tellurene flake with different contacts under illumination with 405nm wavelength LED	44
6.4	Photoresponse of tellurene flake with Pd contact under illumination with 405nm wavelength LED at 11K and 300K	44
6.5	Optical image showing spatial illumination of (a) Bulk channel (b) Lead-1 (c) Lead-2	46
6.6	Spatial photocurrent of tellurene devices with different contacts	46
6.7	Optical image of tellurene flake using polarized light at (a) 0° (b) 80° (c) 110° (d) 180°	47

Chapter 1

Introduction

1.1 2D materials

Two-dimensional (2D) materials are layered material that are one or few atoms thick. They have unique properties in comparison to their bulk counter parts. The discovery of first 2D material, graphene, in 2004 earned Andre Giem and Konstantin Novoselov a nobel prize in 2010 [1]. Graphene is a single layer of carbon atoms arranged in hexagonal lattice. Since the discovery of graphene, a variety of 2D materials such as MoS₂ (molybdenum disulphide), h-BN (hexagonal boron nitride), WSe₂ (tungsten diselenide), etc. have been synthesized and studied. Each of these 2D materials have unique properties making them suitable for certain applications.

Graphene is known for several of its properties such as exceptional mechanical strength, thermal and electrical conductivity, extremely high mobility, etc. However, the semi-metallic behaviour of graphene makes it difficult to be used in electronic devices [1]. Other TMDs like MoS₂ have semiconducting property and have huge potential to be used in modern day transistors.

Different 2D materials can be stacked on each other as shown in fig.1.1 to get new emergent properties. These structures are called van der Waals heterostructure because of the van der waals force between layers [2]. This technique can be used to engineer the desired property out of such 2D materials.

The unique properties of 2D material make them most suitable for practical applications. For example, graphene is being explored to be used in high-speed electronics, energy storage devices, sensors, etc. 2D materials can be used for various application such as flexible electronics, wearables, high efficiency solar cells, high-speed electronics, gas sensing, nanoscale

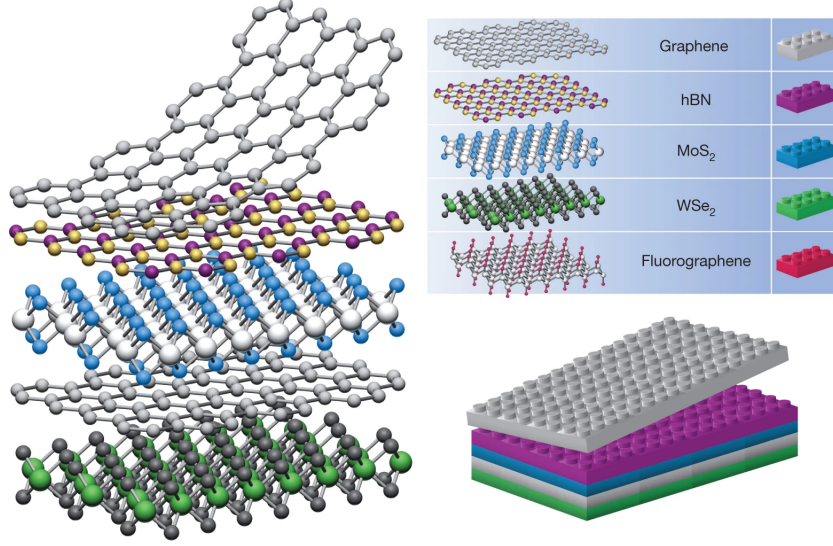


Figure 1.1: Schematic of 2D van der Waals heterostructure as lego blocks [3]

capillaries, catalysis, biomedicine, LEDs, etc [2].

There has been a significant progress in this field. However, despite such a progress there are still many challenges to face. Synthesis of high quality 2D flakes is the most challenging one. Lot of research has to be carried out to make these materials suitable for commercial application. There are several sub categories of 2D materials like transition metal dichalcogenides (TMDs), MXenes, Xenes, etc.

TMDs are a family of compounds with the general formula MX_2 , where M is a transition metal (Mo, W, Nb, etc.) and X is a chalcogen (S, Se, Te, etc.). In these layer structured compounds layer of metal atoms are sandwiched between layers of chalcogen atoms [4]. Similarly, MXenes are a family of compounds that have the general formula of $\text{M}_{n+1}\text{X}_n\text{T}_x$, where M is an early transition metal (Ti, V, Nb, etc.), X is carbon or nitrogen with n being between 1 to 3 and T_x is a surface termination group (O, OH, F, etc.). These also have a layered structure with a layer of metal atoms sandwiched between two layers of carbon or nitrogen atoms [5]. These are just some of the 2D materials discovered so far, there are a lot more to be explored and discovered.

1.2 X-enes

X-enes are newly found monoelemental single or few layers of a group IIIA-VIA [6]. Graphene, the first member of 2D materials family, is the first discovered X-ene. X-enes

have garnered significant attention in the recent time. With increasing interest in X-enes, researchers have uncovered new members in this family. Some examples of X-enes include silicene (silicon), phosphorene (phosphorus), germanene (germanium), stanene (tin), etc. The exploration of Xenes started with the successful isolation of silicene, 2D form of silicon, in 2010. As the family of Xenes grows, researchers have recently started giving attention to Tellurene. From silicene to tellurene, Xenes seem to be a great category of material for electronic and optoelectronic applications.

1.3 Tellurene

Tellurene is one of the recent addition to the family of X-enes. It is a few layer form of group-VI element Tellurium. 2D Tellurene was experimentally realized for the first time in 2018 [7]. Tellurene is a p-type semiconductor with intriguing properties such as environmental stability [8], high carrier mobility [7], bandgap tunability [9], photoconductivity [10], thermoelectric [11], piezoelectric [12], etc [13, 14, 15, 16]. These properties make tellurene a potential material for future device integration. Due to its recent experimental realization, very less is known about it as compared to graphene. Unlike conventional 2D material, tellurene is made of atomic chains in triangular helix, which are stacked and held together by van der Waals force [10]. Fig.1.2 shows the crystal structure of tellurene.

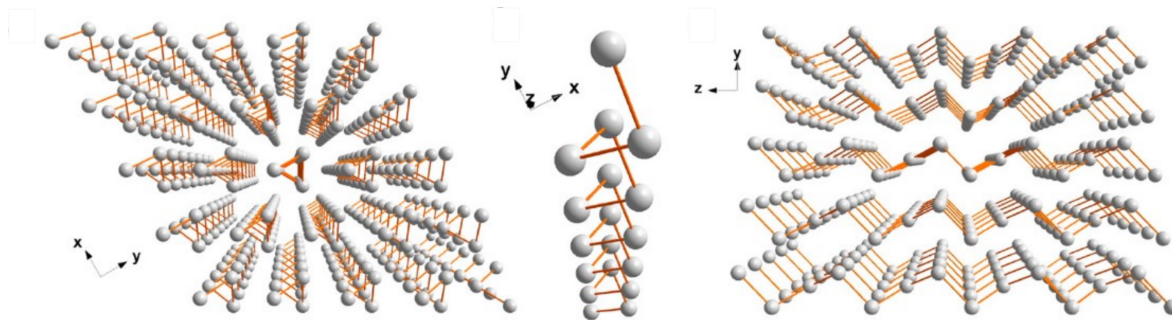


Figure 1.2: Schematic of crystal structure of tellurene viewed from different directions [10]

Numerous theoretical and computational reports have been published predicting the properties of tellurene [17]. Tellurene in its monolayer form is calculated to possess a direct bandgap of 1.04 eV which can be tuned down to indirect gap of 0.38 eV in its bulk form [9]. It was also predicted that the bandgap could be varied by applying strain [18]. Recent experiments have also realized these predictions. The small bandgap of tellurene makes it a very potential material for use in IR detection. Tellurene is found to have high respon-

sivity in a wide range of wavelengths from mid IR to visible [10]. Tellurene has properties comparable to that of black phosphorous with the added benefit of being highly air-stable [8].

Based on the initial calculations and experimental evidences, tellurene seems to have huge potential to be applied in photodetectors, FETs, piezoelectric devices, solar cells, etc. Wang et al. reported a high performing flexible photodetector made of tellurene [23]. They found that the response changed minimally even after 100 bending cycles. Similarly, Ye et al. reported high speed FETs realized using tellurene flakes [7]. The FETs had an on/off ratio of about 10^5 and field-effect mobility around $700 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

Most of the research that has been reported has concentrated on the visible and IR response of tellurene. More research is required to assess the potential of tellurene to be used as an ultra-broadband device (UV to mid IR). More work has to be done to improve the performance of tellurene devices. There is a huge scope to study the doping and heterostructure of tellurene. There are some computational papers that predict tellurene/ WS_2 heterostructure to have a high efficiency as a solar cell [19]. Very less research has been done involving strain.

Another most important aspect to consider while trying to improve the efficiency of devices is contact engineering. Very less work has been done in this field for tellurene devices. There are few computational reports suggesting various contacts to enhance the efficiency of tellurene FETs [20]. In this work we have tried to experimentally analyse different contacts to tellurene and study its implications. Through this work we try to understand deeper about the intrinsic properties of tellurene by eliminating the effects of contacts. We also try to understand the properties of contacts to harness it for practical application.

Chapter 2

Synthesis

2D materials can be synthesized in various ways namely CVD, PVD, PLD, exfoliation, chemical ways, etc. Each method has its own pros and cons. Tellurene since its prediction long back, was tried to be synthesized using different techniques. But unfortunately, due to its inherent anisotropic structure, synthesizing 2D sheets was not very feasible. However, in 2018 a hydrothermal technique was discovered which could synthesize high quality large sheets of Tellurene. In this chapter we will discuss the various techniques used for the synthesis of Tellurene.

2.1 Physical Vapor Deposition

Physical Vapor Deposition (PVD) is a common technique used to synthesize 2D materials. PVD is a technique in which the source material are transformed into vapor using a physical process (such as heating or bombardment). The produced vapor is then deposited on desirable substrate. There are many PVD techniques such as, Pulsed Laser deposition, Sputtering, Thermal Vapor Deposition, etc. There were many tries to synthesize 2D Tellurene using such PVD techniques. Despite initial success in some cases, none of them were able to grow large scale thin films efficiently.

2.1.1 Physical Vapor Transport

Recently, Apte et. al. used PVT to synthesize Tellurene on SiO_2 [21]. They were able to synthesize tellurene of thickness $< 7\text{nm}$ with an area of $50\ \mu\text{m}$. They used Ar/H_2 carrier gas to transport Tellurium vapors, formed by heating at $650\ ^\circ\text{C}$, to deposit on Si/SiO_2 substrate

placed down the stream. They were able to achieve thinnest flake of thickness 0.85 nm corresponding to 3 layers. They further characterized the as-grown flakes using TEM and STEM to check the crystallinity of the flakes.

2.1.2 Thermal Evaporation

In 1960s Zhao et al. after long endeavours synthesized high quality Te film using this method [22]. Te pellets were used as source to deposit 2D tellurene flakes. They were able to deposit 4-53 nm of tellurene film at low pressure and temperature in an Edwards Coating System. They noticed that the substrate temperature had a significant effect on the quality of films synthesized. They were able to monotonically increase the average area of domain from zero to $25 \mu m^2$ by decreasing the temperature of the substrate from room temperature to - 80 °C.

2.2 Molecular Beam Epitaxy

Molecular Beam Epitaxy (MBE) is a method of thin film deposition. MBE works at high to ultra-high vacuum. The typical deposition rate is below 3000 nm per hour, which allows epitaxial growth of films. Recently, tellurene was synthesised successfully on mica and graphene substrates using MBE. Highly crystalline tellurene flake of 30-80nm lateral dimension was grown on mica substrate. Similarly mono and few layer tellurene flakes of high quality were also grown on graphene substrate. However, it seemed difficult to increase the lateral size of the obtained flakes in this method [23].

2.3 Liquid Phase Exfoliation

Liquid phase exfoliation as the name suggests, uses a liquid medium to exfoliate a crystal. The efficiency of exfoliation would depend on various factors such as sonication energy, solvent used, duration of sonication, etc. Xie et al. reported that LPE can be used to obtain ultrathin tellurene flakes [24]. Tellurium powder was dissolved in IPA and probe-sonicated to exfoliate them. As per their report, they obtained flakes of 50-150nm lateral dimension with a range of height. Although this method could attain monolayers, it is difficult to scale and the lateral dimensions are very small.

2.4 Hydrothermal Synthesis

Hydrothermal Synthesis is a technique used to synthesize crystals using the solubility of chemicals in water at high temperature and pressure. The growth happens inside a pressure container called “autoclave”. This method provides a substrate free synthesis technique. In this method the flakes grown remain suspended in the solution which can be purified and drop-casted on any desirable substrate. The yield of this techniques remains higher than other techniques. In 2018, Wang et. al. were able to successfully synthesize high quality Te flakes using this technique [7]. This kindled the interest of 2D society in Tellurene flakes.

We used a similar technique to synthesize flakes for our study in this thesis. We mixed calculated amounts of various chemicals like 0.6g of PVP (Poly Vinyl Pyrrolidone - 40k molecular weight), 6.4 ml of Distilled water, 18.4mg of Na_2TeO_3 (Sodium Tellurite), 0.64ml of Ammonium hydroxide and 0.34ml of Hydrazine hydrate. The mixture was mixed well and transferred into an autoclave. The autoclave was sealed and kept for heating at 180°C for 18 Hours. We hypothesize that the precursors inside the autoclave come together to form quantum dots of tellurium which grow in one direction to form nanowires. These nanowires come together to form 2D sheets of tellurene. The schematic of hypothesized growth process is shown in fig. 2.1.

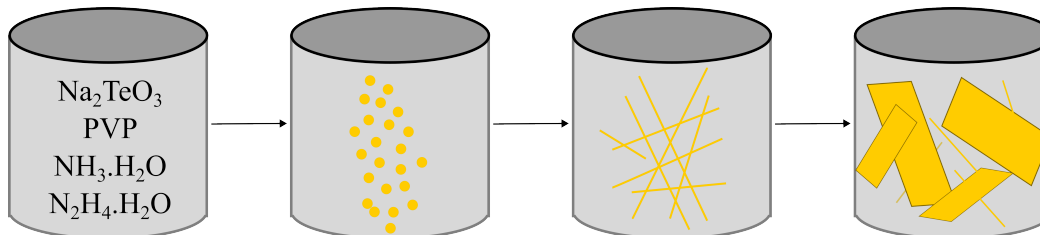


Figure 2.1: Schematic of hypothesized growth process inside an autoclave from precursors to quantum dots to nanowires to 2D tellurene sheets

The autoclave is let to cool down naturally. After reaction the obtained black solution is transferred to a centrifuge tube. The solution is cleaned using distilled water and ethanol twice each by centrifuging at 7000 rpm for 5 minutes. The obtained sediment is further dispersed in ethanol. This final solution can be drop casted onto any desirable substrate whenever needed.

Chapter 3

Structural Characterization

After synthesis, the characterization of these materials is the next step. These materials, having only few layers, exhibit significantly different properties from their bulk counterparts. Structural characterization includes a variety of techniques each exploring a different aspect of the material. Optical imaging is the most fundamental technique used. Various other techniques include SEM, AFM, HR-TEM, EDX, XRD, XPS, STS, etc.

Before delving into the electrical properties of the synthesized tellurene flake, it is important to verify the composition, phase, purity, crystal structure to build a strong base for our further exploration. In this chapter, we present the comprehensive structural characterization of the synthesized crystals. The synthesized crystals were drop casted onto SiO_2 and their structural properties were studied in depth.

3.1 Optical Images

Optical images are the primary characterization of any 2D material. The obtained flakes are observed under a microscope at varying magnification to understand the morphology of the flake. In addition we get a qualitative idea about their height using dark field images. In comparison to bright field imaging, in dark field imaging the collection of scattered light occurs from the edges of the lens. In this study we used Nikon Eclipse LV15ON microscope. The as-grown flakes were observed under microscope. We observed that majority of the flakes have a trapezoidal structure. Along with 2D tellurene sheets, we also observed the presence of nanowires and nanorods which support the hypothesised growth process. Few bright and dark field optical images are shown in fig. 3.1. A varying height was observed in the dark field imaging.

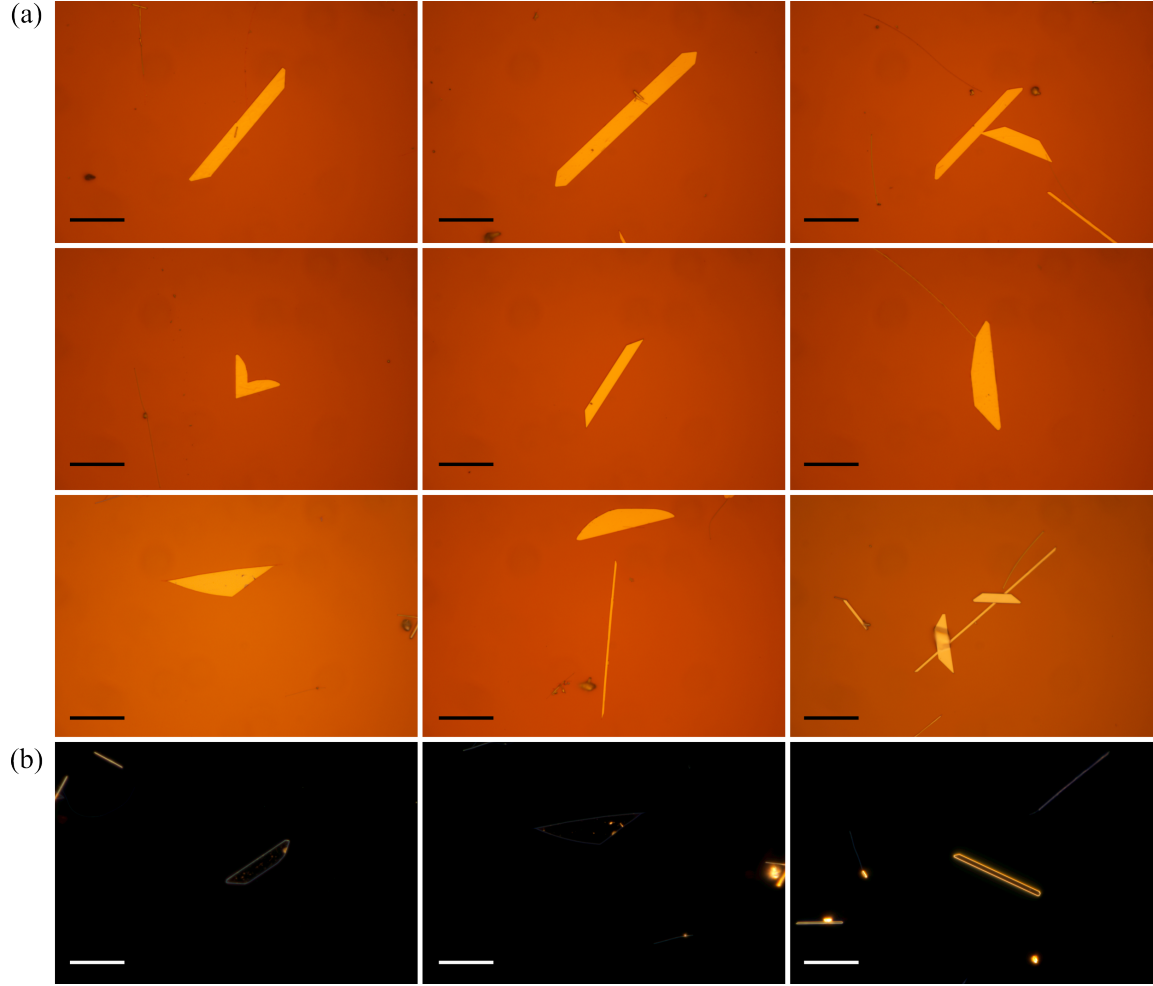


Figure 3.1: (a) Bright field optical images of as-grown tellurene flake under 100x magnification showcasing different structures (b) Dark field optical images of as-grown tellurene flake under 100x magnification (scale 20um for (a) and (b))

3.2 Scanning Electron Microscopy

Scanning Electron Microscope (SEM) is a very powerful technique used to study the morphology of solid structures especially 2D materials. It uses a focused beam of electrons to scan the surface of sample and generates various signals that contain information about its topography. In SEM electrons are produced using an electron gun and accelerated down a column. The beam of electrons are focused to a fine point using magnetic lenses. This focused beam falls on the surface of the sample and some electrons bounce back while some get emitted by the sample. These are called backscattered electrons and secondary electrons respectively. A detector collects the secondary and backscattered electrons and converts

them into an electrical signal which is then displayed as an image on the screen. In our work we used a Zeiss Crossbeam - 350 FIB-SEM for imaging at 3kV acceleration. The SEM images of the as-grown flakes are shown in fig. 3.2. We observed the presence of nanowires and 2D sheets supporting our observation in optical microscope.

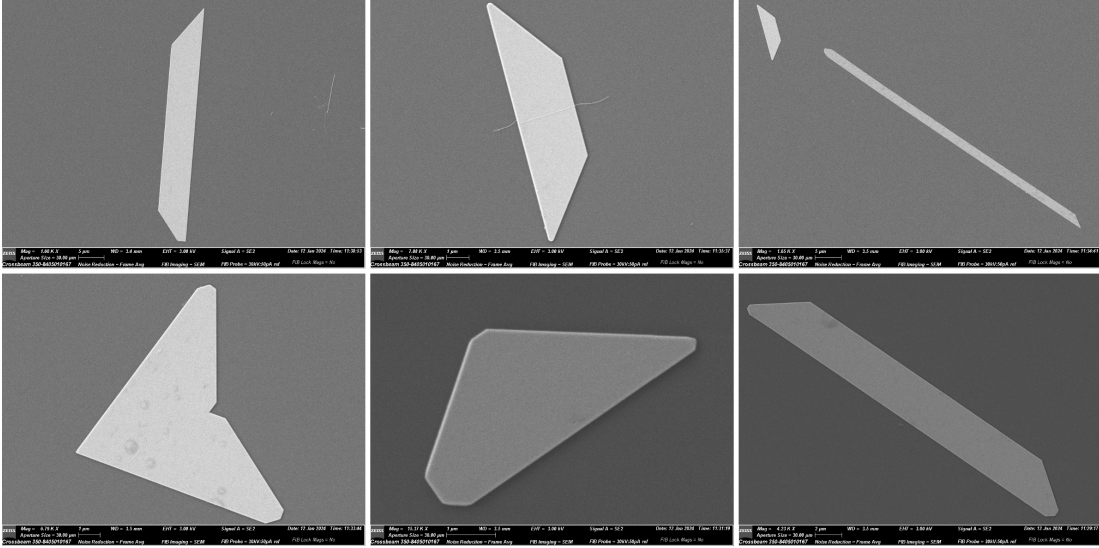


Figure 3.2: Scanning Electron Microscopic image of the as-grown tellurene flake showing different morphologies and smooth surfaces

In addition, from SEM images we observed that the surface of the as-grown flakes are clean and the flakes have a sharp edge. The average width and length of the flakes were estimated to be around $2 \mu m$ and $35 \mu m$. We also observed that the flakes have a considerable thickness. The thickness of nanowires were estimated to be around 70 nm.

3.3 Raman Spectroscopy

Raman Spectroscopy is a very powerful tool for studying the vibrational modes of materials and especially 2D materials. Due to inelastic scattering the scattered electrons undergo a shift in frequency. This shift is proportional to the difference in energy state of initial and final vibrational states of the sample and is called the raman shift. Raman spectroscopy is such a powerful tool that it can provide insights not just on structure, composition and phase of the sample but also on the strain, defects and number of layers.

In Raman scattering, a monochromatic laser beam is incident on the sample. The scattered light is collected by a lens and sent to a spectrometer. The spectrometer analyses the

intensity of light at different wavelengths. While Rayleigh scattering gives rise to no change in the wavelength of incident and scattered light, raman scattering causes the scattered light to be at higher (anti-stokes) or lower (stokes) energy from the incident light. By plotting the intensity of raman scattered light versus raman shift, we get complete information about the vibrational modes of the sample.

In this work we used an IndiRam CTR-300C raman spectroscope with 532 nm laser for all our raman measurements. We observed three prominent peaks for tellurene at 93 cm^{-1} , 121 cm^{-1} and 142 cm^{-1} . The peak at 93 cm^{-1} corresponds to E^1 transverse phonon mode and those at 121 cm^{-1} and 142 cm^{-1} correspond to A_1 and E_2 modes respectively. Decreasing thickness of the flake causes a blueshift in both the A_1 and E_2 modes. Fig.3.3a shows the raman spectra of the as-grown flakes and fig. 3.3b shows a schematic of the vibrations that leads to the above mentioned peaks.

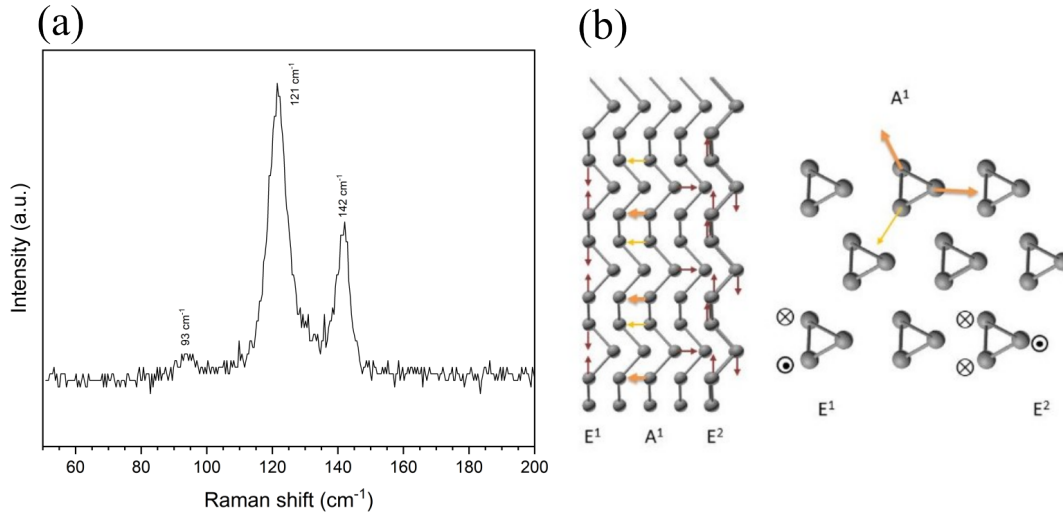


Figure 3.3: (a) Raman spectra of the as-grown tellurene flakes. (b) schematic of various vibration modes corresponding to the raman peaks [7]

Fig. 3.4 shows a raman mapping of the as grown flakes. Raman mapping confirms the presence of uniform bonding environment throughout the flake. The obtained raman spectra and mapping confirm the composition, phase and purity of the flakes grown. The obtained peaks match well with those reported in literature [7].

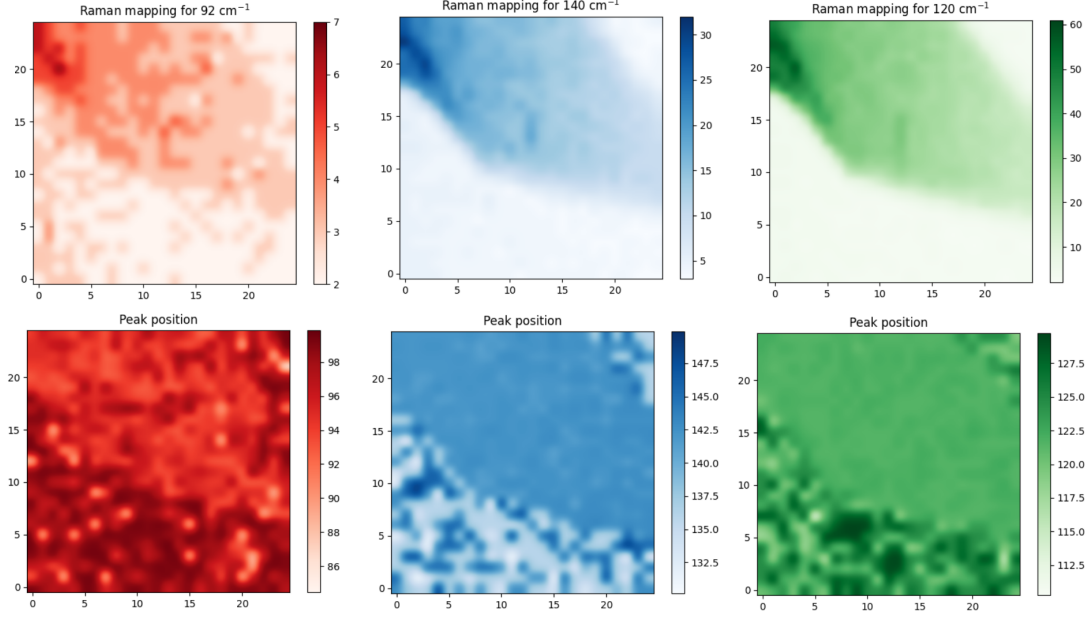


Figure 3.4: Raman mapping of as-grown tellurene flakes corresponding to their three major peaks depicting the intensity and peak position

3.4 Atomic Force Microscopy

Atomic Force Microscope (AFM) is an instrument that uses a sharp tip to probe the surface of the sample. It measures the force between the probe and the surface of the sample. AFM can be used to study the morphology, surface roughness and thickness of the sample. In addition, AFM can also be used to cut, fold or modify 2D materials.

AFM works by measuring the intermolecular force between the sample and the probe. The probe is raster scanned over the surface of the sample. The up and down motion of the tip is monitored by using a laser light reflected off the top of the cantilever tip. The reflected laser is captured by a position sensitive photodetector (PSPD). The PSPD is calibrated to determine the position of the cantilever from the position of the reflected laser beam. AFM can be operated in two modes, namely, tapping mode and contact mode. In tapping mode, the cantilever is oscillated at a high frequency and the tip does not come in contact with the sample. Whereas, in contact mode the tip moves while being in contact with the sample surface, increasing the probability of damaging the sample.

In this work, AFM measurements were made using nanosurf AFM. This AFM has a resolution of 1 nm. The average height of the obtained flakes were estimated to be around 35 nm. Fig. 3.5 shows an AFM image of a newly synthesized flake. The surface of the

flakes appear smooth and clean supporting our observation in SEM. The surface roughness is minimum and the flakes have a sharp boundary.

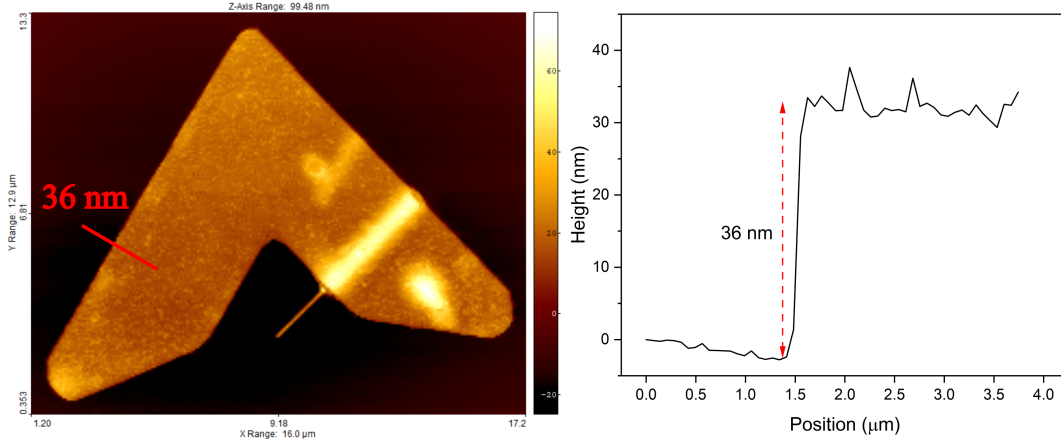


Figure 3.5: Atomic force microscope image of a tellurene flake and its trace showing 36 nm of height

3.5 High Resolution Transmission Electron Microscopy

High Resolution Transmission Electron Microscopy is used to study the properties of materials by focussing and transmitting high energy electrons through the material. 2D materials being very thin, HRTEM can be used to study their atomic arrangement. HRTEM just like SEM also has an electron gun that produces electrons and accelerates it down the column. A series of apertures and magnetic lenses are used to focus the electron beam and pass it through a thin sample. The electrons transmit through the thin sample and reach the detector, which further converts it into an electrical signal. The interaction of electrons with sample creates a contrast in the image. The contrast depends on the atomic number, crystal orientation, thickness, etc. In addition to imaging, HRTEM can also be used to get diffraction data. While part of the electrons get transmitted through the sample, the other part get diffracted. These diffracted electrons can be collected to get information about the crystallinity of the sample. This is called “Selected Area Electron Diffraction (SAED)” mode of HRTEM.

In this thesis we used a JEOL JEM 2200FS, Japan equipped with 200 keV field emission gun (FEG). Fig.3.6a shows a HRTEM image of the as-grown flake. A part of the HRTEM image was Fourier transformed and processed to remove noise. Fig.3.6b shows an inverse

fast fourier transformed image of the processed image. The crystal structure looks clear in the processed image. In addition, fig.3.6c shows the SAED of the flakes. From the HRTEM

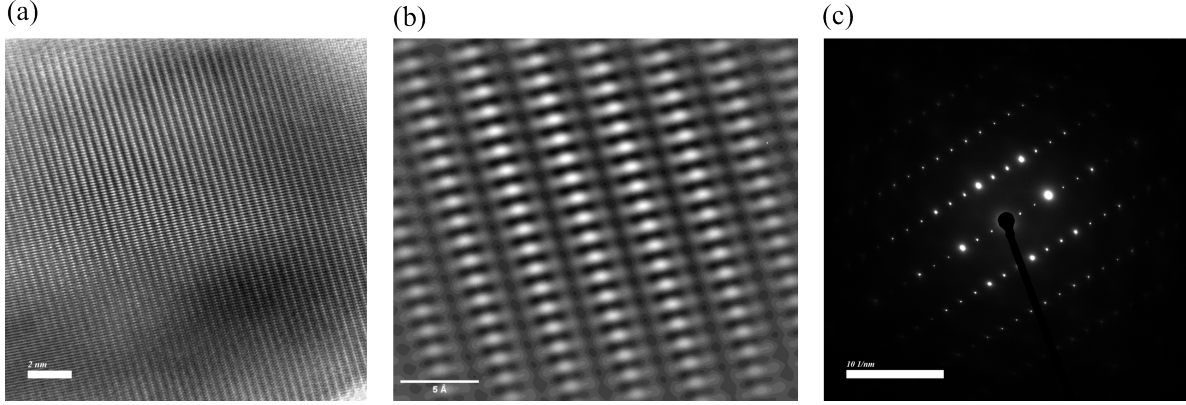


Figure 3.6: (a) HR-TEM image of an as-grown tellurene flake (b) IFFT of a selected area noise reduced FFT of the TEM image (c) SAED pattern of the as-grown flake

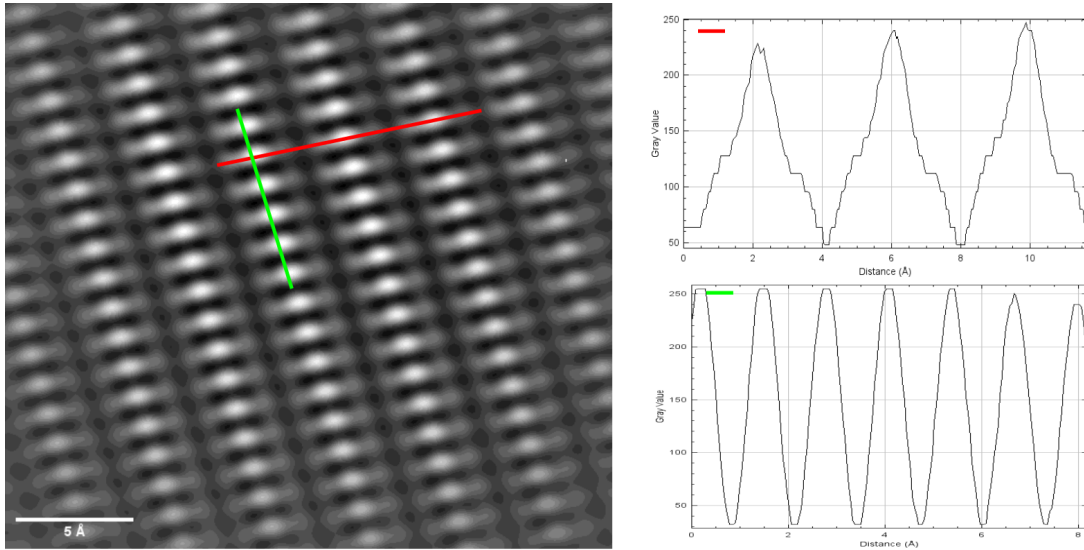


Figure 3.7: Graph depicting the interatomic separation in two direction

images of the flake we estimated the interatomic spacing of Tellurene to be $3.5\text{\AA}$ perpendicular to the chains as shown in fig.3.7. The red line profile in fig. 3.7 shows the presence of 3 atoms in each chain confirming the trigonal helical crystal structure of the chains. The SAED pattern confirms the high crystallinity of the synthesized flakes. The obtained images also confirm minimal presence of defects in the as-grown flakes.

3.6 Energy Dispersive X-Ray Analysis

Energy Dispersive X-ray Analysis (EDX) is used to determine the elemental composition of any material. EDX can be coupled with SEM or TEM. From EDX data, we could determine the elemental composition and purity of the synthesized sample. The high energy electrons incident on the sample excite the inner shell electrons to higher levels. These excited electrons subsequently relax to lower levels emitting X-rays which are characteristic of the elements. In SEM and TEM, a specialized detector is used to capture the X-rays emitted from the sample. This signal is analyzed to understand the elemental composition of the sample. Fig.3.8b shows an EDX analysis of the as grown flakes taken in SEM. Fig.3.8a shows an EDX analysis of the as-grown flakes taken in TEM.

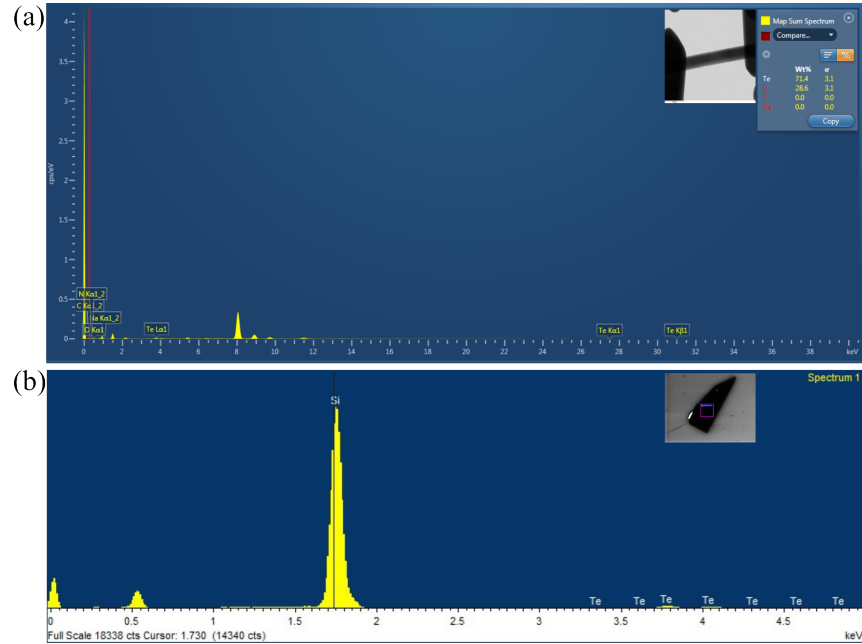


Figure 3.8: (a)EDX of the as-grown tellurene flakes obtained using HR-TEM (b)EDX of the as-grown tellurene flakes obtained using SEM

From the EDX analysis we confirm that the samples prepared are of high purity. In addition to Tellurium peak, the SEM-EDX has peaks of Silicon and Oxygen because the flakes were drop casted on SiO₂ substrate for analysis. Similarly TEM-EDX shows peaks of Copper and Carbon in addition to Tellurium because the TEM grid onto which the flakes were drop-casted had carbon back and copper grids. The absence of carbon and copper peaks in SEM-EDX and absence of silicon and oxygen in TEM-EDX confirms that these peaks come from the substrate and not from the flakes. However, it is also important to

note that oxygen and carbon peaks in EDX may also arise due to partial surface oxidation and atmospheric dust respectively.

3.7 X-Ray Diffraction

X-Ray Diffraction is a very vital tool to understand the composition and phase of materials. However, techniques like Powder XRD (PXRD) and Single crystal XRD are not suitable for 2D materials (monolayers and bilayers). For 2D materials, glancing incidence XRD is commonly used. However, in our case, since the obtained flakes are few-layers thick, we used PXRD for our study. PXRD works on the basis of Bragg's law. In PXRD, the material (usually crystal) under study is illuminated at an angle with monochromatic X-ray. These rays, according to Bragg's law, undergo constructive and destructive interference at different angles to form a diffraction pattern characteristic of the lattice spacing. The graph of intensity versus angle of incidence provides us information about the crystallinity, phase and composition of the material.

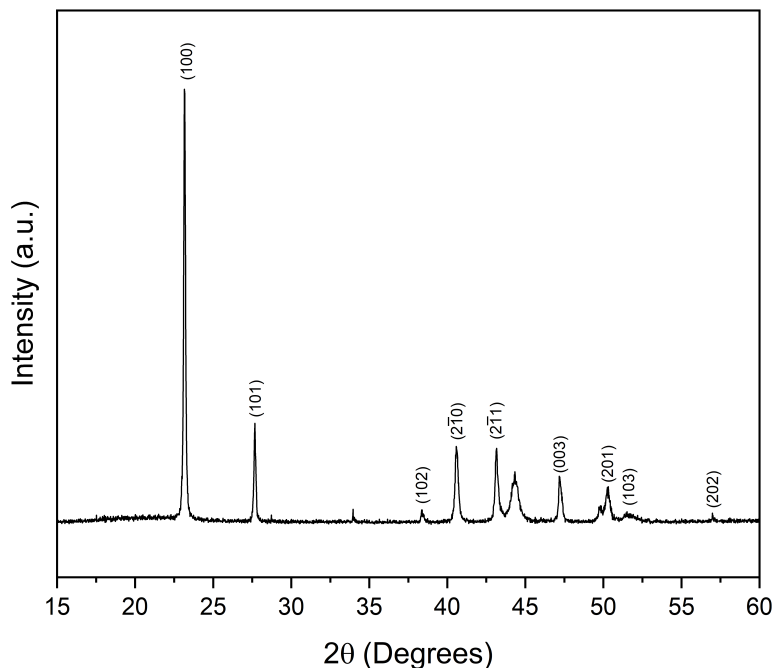


Figure 3.9: X-ray diffraction pattern of the synthesized tellurene flakes

In this study we used a Malvern Panalytical Empyrean Series - III PXRD system. Fig.3.9 shows the PXRD data of the as-grown flakes at room temperature (298 K). The obtained data reveals distinct diffraction peaks. These peaks are in good agreement with the literature

values for tellurene [25]. This confirms the purity and crystallinity of the obtained flakes. PXRD data obtained at a temperature of 130K, shows no changes from the room temperature data. This ensures the absence of any structural change in the material with temperature down to 130 K.

3.8 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is an important tool used to characterize 2D materials. XPS provides details about the composition and chemical state of the material under study. XPS is a highly surface sensitive technique and provides information about the surface chemistry and bonding environment of the material. In XPS, the material under study is incident with X-rays of specific energy. The core electron of the material get excited and ejected due to the X-ray. The kinetic energy of each photoelectron is related to its binding energy. By measuring the kinetic energy of these photoelectron, the composition of the material can be determined. In this study we used Thermo Scientific K-Alpha⁺ X-ray

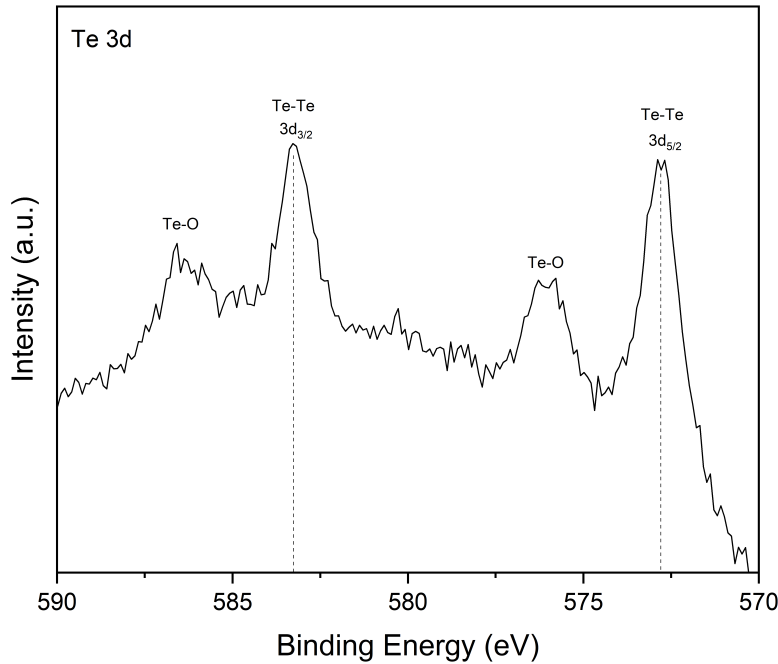


Figure 3.10: X-ray photoelectron spectroscopy of the as-grown tellurene flake

Photoelectron Spectrometer system. It uses Al K-Alpha X-ray of energy 1486.6 eV. Fig.3.10 shows XPS spectra of Te 3d orbital. The XPS spectra shows distinct peaks corresponding to Te-Te bonds at 572 eV and 583 eV. However, we can also observe peaks at 575 eV

and 586 eV which correspond to Te-O bonds. Presence of Te-O bond may be due to mild atmospheric surface oxidation or due to mild oxidation during hydrothermal growth. The XPS data complements other characterizations done and provides a strong idea about the chemical purity of the as-grown flakes. The obtained XPS data is in good agreement with the literature [25].

3.9 Scanning Tunnelling Spectroscopy

Scanning Tunnelling Microscopy (STM) and Scanning Tunnelling Spectroscopy (STS) are powerful tool used to image and probe the electronic properties of materials at atomic scale. STM and STS provide valuable insight about the surface morphology, crystal structure, local density of states, etc. In STM and STS, a sharp conducting tip is placed very close to the material under study (typically few angstroms). When a bias is applied between the tip and the material, a tunneling current flows between the tip and the material because of the electrons tunnelling through the vacuum (or air medium) barrier in between. The conducting tip is raster scanned, maintaining a constant current, on the surface of the material to image and study its electronic structure. In STS, the tunnelling current at a point is measured as a function of bias voltage. The rate of change of tunnelling current with respect to bias voltage is proportional to the local density of state. Hence, STS can be effectively used to probe the density of states and find the band gap of the sample.

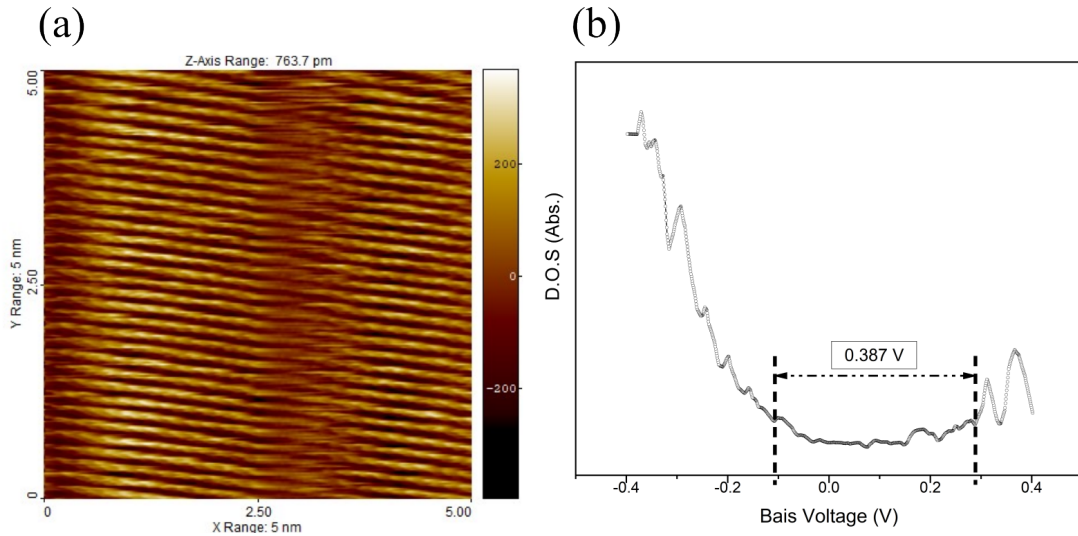


Figure 3.11: (a) STM image of a tellurene flake (b) STS of a tellurene flake showing a bandgap of 0.39eV

In this thesis we used nanosurf easyscan 2 STM in ambient conditions. The instrument was calibrated using graphene flake. After calibration the angle between the unit vectors of graphene lattice were estimated to be around 122° . Fig.3.11a shows an STM image of Te flake and Fig.3.11b shows the STS data obtained.

An STS data was obtained by taking mean of 25 IV characteristics at the same point. From the obtained data, the band gap of tellurene is estimated to be around 0.38 eV. This is in excellent agreement with computationally calculated bandgap of few layer tellurene [7, 26]. The STS data from different points showed minimal change in bandgap. This confirms that the synthesized flakes have uniform electronic structure.

Chapter 4

Device Fabrication

Two dimensional (2D) device fabrication is a crucial step in the integration of 2D materials in modern electronic and optoelectronic devices. After synthesis and basic characterization of the flakes, it is necessary to transfer the flakes onto desired substrate pattern 2D devices on them to do electrical characterization. Different patterns like 2-probe, 4-probe, hall bar, van der Pauw, transfer length, etc. can be made. Each pattern has its own special use. For instance, 2-probe is the simplest device geometry for electrical characterization. Though 2-probes are most efficient for commercial device integration, they measure the combined property of the material and contacts instead of just the material. On the other hand, 4-probe can be used to eliminate the effect of the contacts and study the property of the flakes. 4-probe is usually used to study the resistivity of the material without the effect of contact resistance. The van der Pauw pattern is used to study the anisotropy of the material by measuring various properties in different directions.

In making such devices, lithography plays an inevitable role. There are various lithography techniques such as optical lithography, electron beam lithography, extreme ultraviolet lithography, X-ray lithography, etc. These techniques use different types of electromagnetic waves to expose patterns on substrates. Each technique has its own pros and cons. While it is essential to get high resolution, it is also important to preserve the integrity of 2D materials. The choice of pattern and the lithography technique largely depends on the requirements.

After these patterns are made, metal needs to be deposited on these patterns to bridge a contact between the 2D and 3D world. Metal deposition can be done using various techniques like thermal vapor deposition, sputtering, electron beam evaporation, etc. Hence, to fabricate a good device, it is essential to carry out all these steps: synthesis, transfer to desired substrate, lithography, metal deposition and liftoff in a very careful manner.

4.1 2D Transfer

Most often the flakes on which devices have to be made are not on desired substrate. 2D transfer methods are techniques for transferring 2D materials from growth substrate to the desired substrate. Transfer of 2D materials is essential because most often, direct growth of 2D materials on desired substrate is challenging. There are various transfer techniques such as: dry transfer, wet transfer, drop-casting, etc. In this study we used mostly drop-casting and occasionally dry transfer also.

4.1.1 Drop-casting

Drop casting is the easiest transfer technique. In cases where the material is suspended in a liquid medium (like water, ethanol, IPA, etc.), drop casting can be used. In drop casting, a drop of the 2D material suspended solution is dropped on the desired substrate and is let to evaporate. After evaporation of the liquid, the 2D materials get deposited on the substrate. The advantage of this method is that it is simple, low cost and is easily scalable. However, the drawback of this technique is that it results in random and non-uniform distribution of the 2D flakes and that it can only be used for materials that can be suspended in some solution. Drop casting can be used for various 2D materials such as Graphene, MoS₂, WS₂, CsPbBr₃, etc.. In this study, since tellurene is suspended in ethanol, drop-casting is used to transfer the flakes from liquid medium to SiO₂/Si substrate for studying.

4.1.2 Dry Transfer

Dry transfer is another technique to transfer 2D materials. In dry transfer, a polymer or a stamp is attached onto the flake on the growth substrate. The polymer is slowly peeled off with the 2D material sticking to it. The stamp with the flake is aligned onto the target substrate and detached slowly. The advantage of this method is that it can be used to do deterministic transfer. However, the disadvantage being that it needs complicated transfer stage and cannot be scaled easily. Dry transfer can be used for applications that require high quality and clean 2D materials. In this study we occasionally used dry transfer. The schematic of the dry transfer is shown in fig.4.1 We used PDMS as the base and clear nail polish as the polymer layer [29].

Dry Transfer

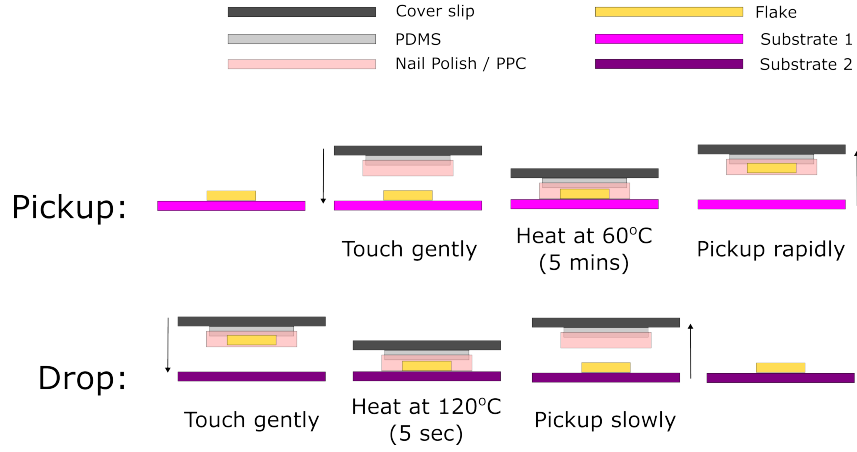


Figure 4.1: Schematic of a dry transfer process

4.2 Photolithography

Photolithography is a technique in which light is used to make patterns on the desired substrate. In Photolithography, a light sensitive material called photoresist is coated over the substrate. There are two types of photoresists, positive and negative. In positive photoresist, the part that is exposed with light becomes soluble in a chemical called developer. While in negative photoresist, the exposed part gets hardened and the remaining part dissolves when immersed in developer.

Photolithography can be done in two ways: shadow printing and projection printing. In shadow printing, the mask is kept in direct contact (or with close proximity) with the substrate and aligned using a mask aligner. In projection printing, the pattern on the mask is projected onto the substrate (kept centimeters away from mask). The line width, or the minimum size of an isolated structure is proportional to the ratio of wavelength of the light used and the numerical aperture of the objective used. Another important parameter is the depth of focus, which is proportional to the ratio of wavelength of the light used and the square of numerical aperture of the objective used. Hence, it is essential to use a higher numerical aperture to get a higher resolution and larger depth of focus.

All devices used in this study have been fabricated using a home-built projection printing lithography setup made using Nikon Eclipse LV150N.

4.3 Metal Deposition

Metal deposition is a crucial step in the fabrication of 2D devices. This step is most essential to make electrical contact with the 2D material. After lithography, a metal is deposited over the entire substrate. The metal due to absence of photoresist in developed regions comes in contact with the substrate or flake and provides connections. Other than contacts, metal deposition is also used to make gate electrodes. Metal deposition can be done using different techniques such as thermal evaporation, sputtering, electron beam evaporator, etc.

4.3.1 Thermal Evaporation

Thermal Vapor Deposition (TVD) is a common technique used to deposit metal in fabrication of 2D materials. TVD is a physical vapor deposition method in which a source material is heated to high temperature to evaporate and form vapor. The vapors are let to deposit on the desired substrate. Very high vacuum is maintained in the chamber to reduce any impurities. In this study we used a very small rate of deposition ($0.1-0.3 \text{ \AA/s}$) to reduce any material damage and very high vacuum of $1\text{E-}7$ Torr.

4.3.2 Sputtering

Sputtering is another common technique used for metal deposition. In sputtering, the sample is loaded into a vacuum chamber that contains the target (material to be deposited). Low pressure Argon is introduced and plasma is generated by applying a high bias between the target material and electrode. The gas particles get ionized and start accelerating towards the target. These particles transfer their kinetic energy to target molecules and eject them from the surface. These ejected target molecules deposit on the desired substrate. In this study, we used low deposition rate ($0.1-0.3 \text{ \AA/s}$) to avoid material damage and a constant pressure of $9\text{E-}3$ Torr of Ar was used for deposition.

4.4 Liftoff

After depositing metal on the developed substrate, it is essential to remove the metal from unwanted places leaving it only in the shape of the desired pattern. A good liftoff is essential to ensure that there is no short circuit. For liftoff, the general process is to immerse the

metal deposited substrate into a stripper solution or any solvent in which the unexposed photoresist dissolves. Acetone, IPA, NMP, DMSO are few such solutions. The unexposed photoresist gets dissolved in acetone and the overlying metal liftsoff without disturbing the metal inside the pattern. Occasionally, due to some reasons, the metal between leads remain undetached. This would lead to short circuit of the device. In such cases, it is recommended to immerse the chip in a beaker filled with acetone and sonicate the solution for 3-5 seconds. However, sonication can cause damage to the samples and can also liftoff the metal from inside the pattern. In this study we immersed the metal deposited substrate in acetone overnight and sprayed with acetone for liftoff.

4.5 Fabrication Recipe

In this study the following recipe was used to fabricate devices:

1. High quality 285 nm SiO_2/Si was cleaned by sonicating in DI water, Acetone and Isopropyl Alcohol (IPA) for 5 minutes each. The substrate was then blow dried using nitrogen gas and baked at 110°C for 1 minute on a hot plate.
2. The substrate was then plasma cleaned using oxygen plasma in Diener Zepto plasma cleaner at 20 watts power for 1 minute.
3. Tellurene flakes dispersed in ethanol solution is drop casted on the plasma cleaned substrate and the solution is let to evaporate naturally
4. The drop-casted substrate is dipped in DI water, Acetone and IPA for 10-15 seconds each and then blow dried to remove any dust deposited on the substrate during evaporation of ethanol.
5. The drop-casted substrates are spin coated with SU-1813 photoresist at 4000 rpm for 1 minute and baked at 110°C for 1 minute.
6. Appropriate flakes are located on the substrate and desired pattern was exposed on them using projection photolithography
7. The time of exposure for lithography was optimised using a dummy substrate.
8. The substrate after exposure is immersed in developer (MF319) for 1 minute to dissolve the exposed parts of the pattern. Subsequently, the substrate is dipped in DI water for 1 minute and then blow dried to stop the effect of developer.

9. The developed substrate were again plasma cleaned using oxygen plasma at low power (10-15 watts) for 10 seconds to ash any thin layer of photoresist still present on the exposed region even after developing.
10. Metal was deposited on these substrate using DC sputtering or thermal vapor deposition.
11. The metal deposited substrates were left in acetone overnight for liftoff. Acetone was sprayed on these substrate to remove the metal from unwanted regions.
12. If the metal didn't go off, rarely a 3-5 second sonication was used to remove metal from unwanted places.

Now the devices are ready for electrical characterization.

Chapter 5

Electrical Characterization

Electrical characterization serves as a powerful technique to understand the potential applications of 2D materials. This involves a set of experiments aimed towards understanding the electrical properties of these novel materials. Various properties such as carrier mobility, carrier type, conductivity, transistor behaviour can be studied. Electrical characterization can give valuable insight about the intrinsic properties of these materials that could help in engineering of devices with enhanced performance and functionality.

In this study, an extensive characterization of the newly synthesized 2D tellurene is carried out. The characterization involved studying the field-effect transistor (FET) characteristics, electrical conductivity, carrier mobility, carrier type, effect of various contacts on the electrical properties, etc. These studies helped to understand the intrinsic properties of tellurene.

In addition, we also studied the electrical properties of tellurene under various conditions to understand its stability and its optimum working condition. Various conditions such as low temperature, vacuum, etc. and various treatments such as vacuum annealing, intense oxygen plasma, etc. were tried. In addition, the contact resistance between different metals and tellurene have been studied in detail to extract crucial information for device optimization.

Remarkably, our study marks the first experimental observation of contact-induced metallization in tellurene flakes. Observation of this novel property of tellurene could play a very essential role in development of new electronic devices. As a whole, the findings from this electrical characterization not only deepened our knowledge about the previously known properties of tellurene, but also opened up new and promising avenues for exploration.

5.1 Output Characteristics

After synthesizing the flakes, a two probe pattern was made on the flakes following the recipe mentioned in section 4.5. 5 nm of Chromium followed by 35 nm of Gold was deposited using thermal vapor deposition. The source-drain IV characteristics was studied in a home-built electrical probe station at ambient conditions using Keithley 2636B source meter. The source-drain IV characteristics is shown in fig.5.1 Contrary to literature [7], the current density observed was very less. In addition, a non-linear IV curve was observed. The non-linear IV curve seemed suggestive of a Schottky behaviour. This led to the hypothesis that the contact resistance between chromium and tellurene might be high.

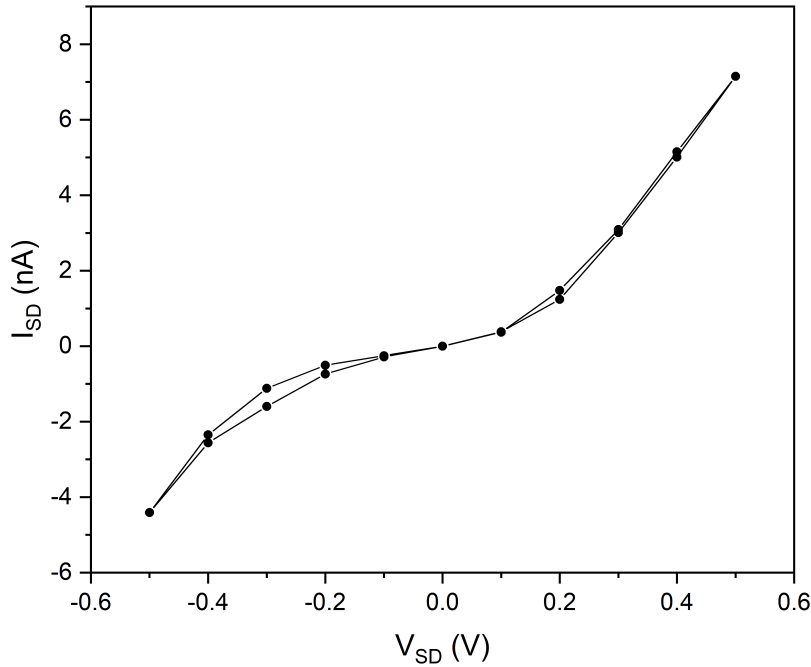


Figure 5.1: Graph showing the output characteristics of 2-probe tellurene device with chromium contact

In order to confirm the same, 2-probe devices with different contact materials such as Cr, Pt, Co, Ni, Al, Ti, Au, Ag, Pd etc. were fabricated. Fig. 5.2 shows the optical image of a 2-probe device.

Materials like Cr, Ni, Al and Ti have a tendency to get oxidised, hence 30nm of such material was capped with 15nm of Gold or Platinum. No capping layer was used for 45nm of Platinum. Palladium being a soft metal would get easily scratched off with probes, hence a capping layer of 15 nm gold was deposited on 30nm of Pd.

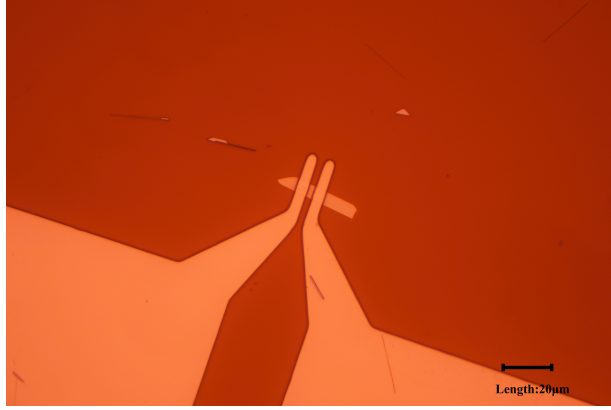


Figure 5.2: Optical image of a fabricated 2-probe device on tellurene flake

In the initial characterization, it was found that Pt, Pd and Ni show a high current density with linear IV characteristics. This could be attributed to lower Schottky barrier due to their higher work function. For a p-type semiconductor, like tellurene, metals with work function closest to (or lower than) the valence band maxima would have lesser Schottky barrier. A graph of IV characteristics for each of Pt, Pd and Ni is shown in fig. 5.3

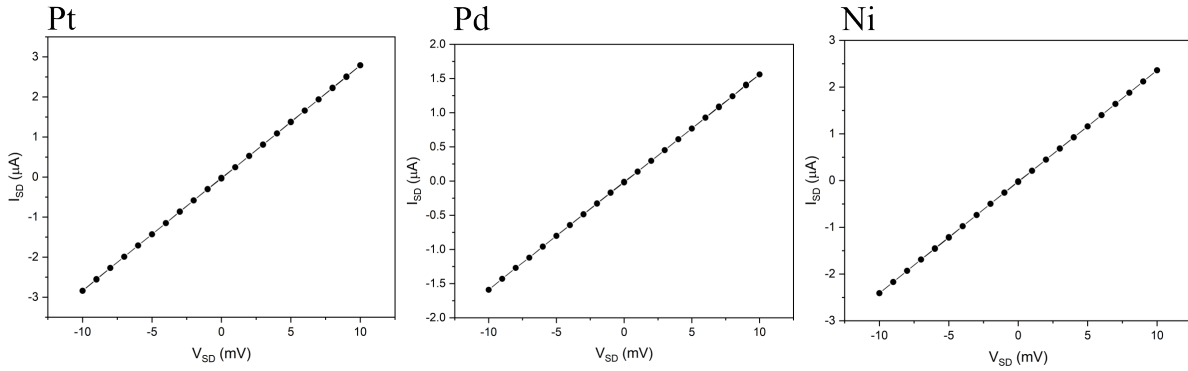


Figure 5.3: Output characteristics of Pt, Pd and Ni contacted tellurene devices

In addition, graphene contact and gold transfer-via-contact were also fabricated and studied. For graphene contact, kis-graphite was exfoliated onto 285nm SiO_2/Si substrate. Incidentally, we found a graphene flake with micro-gap in the middle. The graphene flake was transferred onto a tellurene flake using dry transfer technique as mentioned in section 4.1.2 and thermal annealed for 40 minutes at 175 $^{\circ}C$ to remove any polymer residues. Fig.5.4a shows the optical image of graphene transferred onto tellurene flake. 2-probe device was fabricated on the heterostructure. Unfortunately, graphene contact also gave a non-linear schottky type IV curve as shown in fig. 5.4b

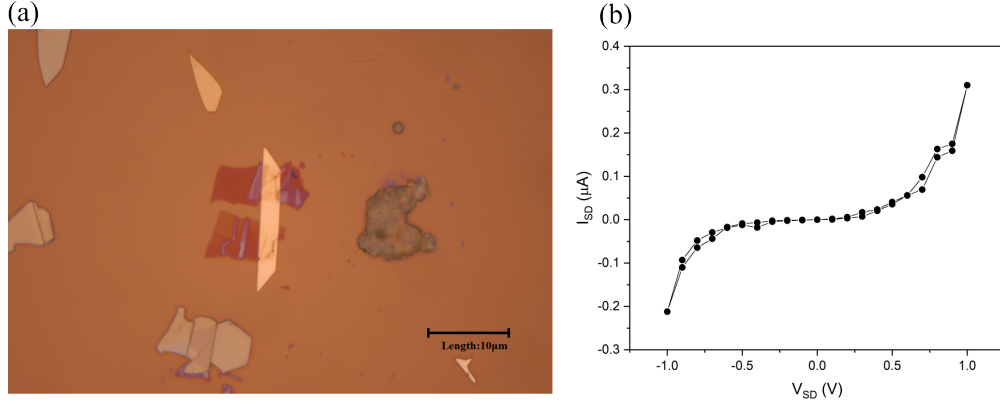


Figure 5.4: (a) Optical image showing the graphene flake transferred onto a tellurene flake (b) Output characteristics of graphene contacted tellurene device

Based on its work function, gold could be a good contact to tellurene. To verify the same, tellurene device with gold contact was fabricated. However, the problem is that the adhesion of gold with SiO_2 is very weak. Hence during liftoff, the pattern would also get washed off. To overcome this issue, we pre-patterned the devices on a bare SiO_2/Si substrate with 3 nm chromium as the adhesion layer and 25 nm gold as the top layer. Tellurene flake was transferred on top of the pattern using dry transfer technique. The top gold layer acts as the contact to tellurene. The output characteristics of tellurene with Au contacts is shown in fig.5.5

It is important to note that both graphene and gold contacts have been realized using transfer. When transferring a flake, a thin van der Waals gap occurs between the flake and contact. This gap might also have an important role in the transport characteristics.

After analysis, we found that Platinum and Palladium show the best performance followed by Nickel and Gold. Hence, for general characterization of the sample properties, Platinum was chosen as the contact material.

5.2 Transfer Characteristics

Field Effect Transistor (FET) transfer characteristics explain the behaviour of 2D materials under the influence of an external electric field applied by a gate electrode. In FETs, a 2D material works as a channel between the source and drain electrode and a gate electrode is placed on the bottom or top of the channel. Using a gate bias, the carrier density in the 2D material channel can be modulated. In other words, gating can be used to electrostatically

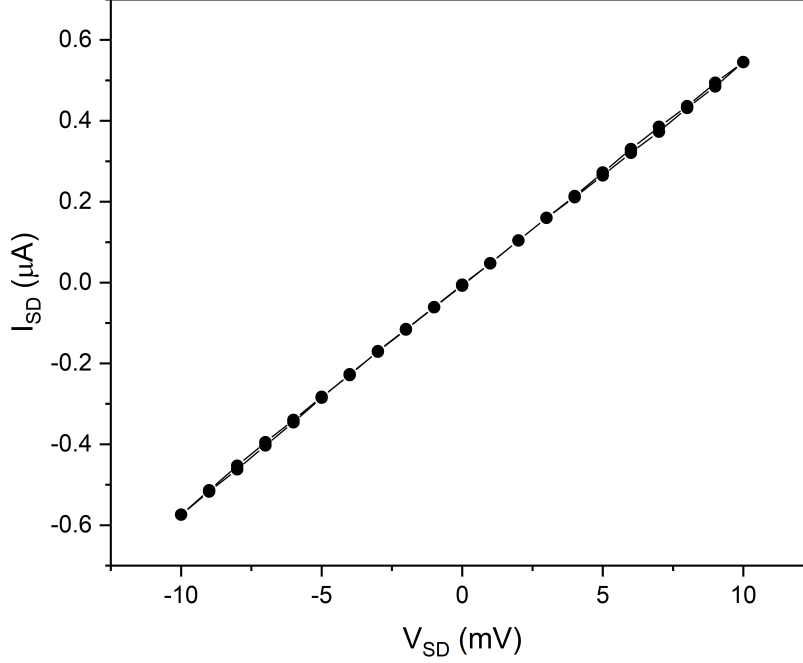


Figure 5.5: Output characteristics of gold contacted tellurene device

dope 2D materials. Tellurene has huge potential to be used in high speed FETs [13, 14, 15]

Gating can give us various important information about the material. Vital parameters such as threshold voltage (V_{th}), mobility, sub-threshold swing (S), on-off ratio (I_{on}/I_{off}), etc. can be measured from the FET measurements. Threshold voltage is the voltage at which the FET switches between off and on states. Mobility is the ease with which the carriers can travel through the channel under the influence of an electric field. Sub-threshold swing is the measure of how sharply the transistor can be turned on or off, i.e. the steepness of the transfer characteristics. As the name suggests, on-off ratio is the ratio of the on-current to off-current of the transistor.

Devices with 2-probe FET geometry with 4 μm channel length were fabricated on tellurene flakes. These devices were made on 285 nm SiO₂/Si substrate. Silicon was used as global back gate. 35 nm of Platinum was sputtered a for usage as contact material. Fig. 5.6 shows the gate dependence of source-drain IV characteristics of the fabricated device.

The threshold voltage was obtained by extrapolating the linear region of the curve. The threshold voltage was estimated to be around 125 V. Similarly, the field effect mobility of the device can be calculated using the following equation:

$$\mu_{FE} = \frac{1}{C_{ox}} \frac{L}{W} \left(\frac{dI_{ds}}{dV_{gs}} \right) \frac{1}{V_{ds}} \quad (5.1)$$

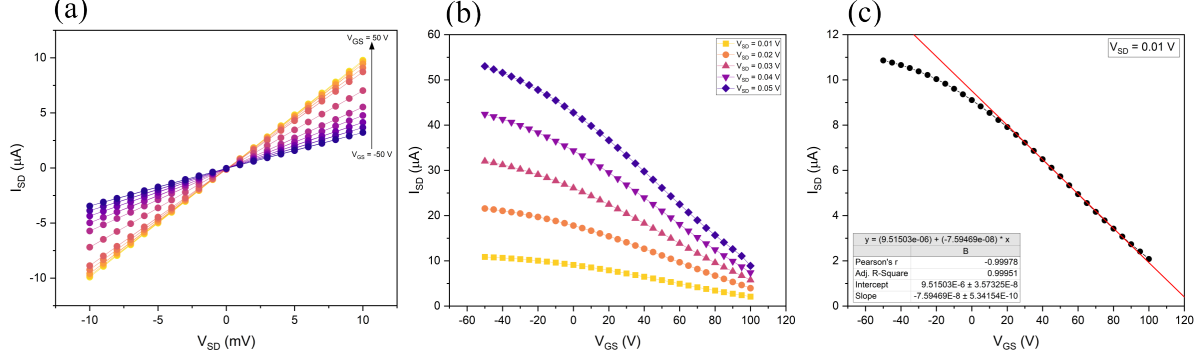


Figure 5.6: (a) Output characteristics of Pt contacted tellurene device with varying gate bias (b) Transfer characteristics of Pt contacted tellurene device (c) Linear fit of the I_{SD} vs V_{GS} curve to obtain mobility and V_{TH}

where, C_{ox} is the capacitance of the oxide layer (SiO_2), L is the width of the channel and W is the width of the channel. The capacitance of SiO_2 layer used is 11.5 nF/cm^2 . Using the above equation, the field-effect mobility of tellurene flakes were obtained to be around $580 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. This value places tellurene in the high-mobility material category. Such high mobility makes tellurene a potential candidate for usage in fast electronic devices. The sub-threshold swing of the device was calculated to be around 103 V/decade . The on-off ratio of the device was around 6. From the obtained curve, we can observe that holes are the majority carriers in tellurene, i.e. it exhibits a p-type behaviour. These findings contribute to the understanding of the material and increases its potential for integration into future electronic devices.

5.3 Stability of Tellurene flakes

2D materials often exhibit remarkable properties under controlled environment, but degrade easily after certain processing. To be able to integrate these materials into modern electronic devices, it is important to understand their stability in detail. In this section we discuss the stability of tellurene flakes after subjecting them to various treatments or conditions. For instance, for a device to be scalable, it must perform considerably well in atmospheric condition. Similarly, such material need to undergo intense cleaning such as with oxygen plasma treatment. Most often, these 2D materials get degraded due to adsorbates that can be removed by vacuum annealing them.

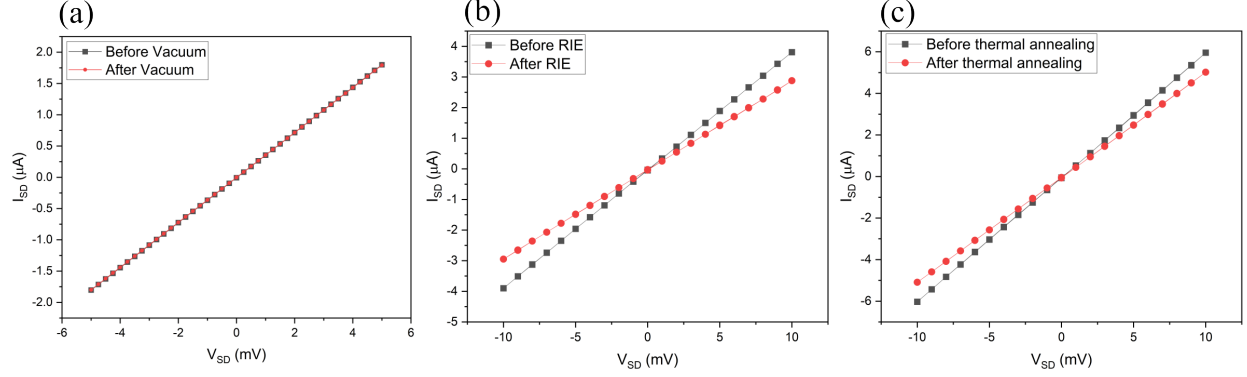


Figure 5.7: (a) I_{SD} vs V_{SD} of tellurene flakes in ambient and vacuum condition (b) I_{SD} vs V_{SD} of tellurene flakes before and after intense O_2 RIE treatment (c) I_{SD} vs V_{SD} of tellurene flakes before and after thermal annealing

5.3.1 Vacuum vs atmospheric condition

The source-drain IV characteristics of tellurene flake were compared in ambient and vacuum conditions. For integration into electronic devices, it is essential to know whether the 2D materials perform well in ambient conditions. Fig.5.7a shows the IV curve in ambient and vacuum condition ($1E-5$ Torr). We observed that tellurene showed minimal change in vacuum and ambient condition. This suggests that devices with tellurene do not need vacuum for efficiency.

5.3.2 After intense oxygen plasma treatment

Few important step in commercial fabrication involve exposure to oxygen plasma. In order to test the tolerance of tellurene flakes, we analysed the source-drain IV characteristics before and after exposed to oxygen plasma. After initial measurements, the device was treated with 120 Watts of Oxygen plasma for 1 minute and studied again. Fig. 5.7b shows the IV characteristics before and after plasma treatment.

Small deterioration in the IV characteristics were noted. However, with the change being not very large, it is safe to assume that tellurene flakes are moderately robust and have huge potential for application in future electronics.

5.3.3 After vacuum annealing

Vacuum annealing is a common technique used to improve the performance of 2D materials by removing adsorbates. Annealing 2D flakes in vacuum result in the enhancement of their

structural integrity. In this study we observed the electrical properties of the flakes before and after vacuum annealing. Basic IV characteristics of the flakes were studied. The flake was then annealed for 40 minutes under a vacuum of 1E-3 Torr at 175 °C. Fig.5.7c shows the IV characteristics before and after vacuum thermal annealing. We observed that there was a very small decrease in electrical current. However, the change is not very significant. From this we could infer that tellurene flakes are robust towards adsorbates. This proves that tellurene is definitely a potential candidate for integration into future electronics.

5.4 Contact resistance

Contact resistance is an important parameter for 2D materials. It plays a crucial role in the performance of electronic devices. Contact resistance is the resistance encountered at the interface of a metal contact and the 2D material. One of the most important cause for high-contact resistance is Schottky barrier. When a metal and semiconductor are brought in contact, band-aligning happens. This might lead to a Schottky barrier, which might lead to inefficient charge injection. High contact resistance leads to increased power consumption and excessive heating at the junctions. This could limit the device performance, mobility, etc.

Measuring the contact resistance is an in important task to understand its effect. A specific technique called Transfer Length Method (TLM) is used to quantify the contact resistance. In TLM, a pattern as shown in fig.5.8 is made.

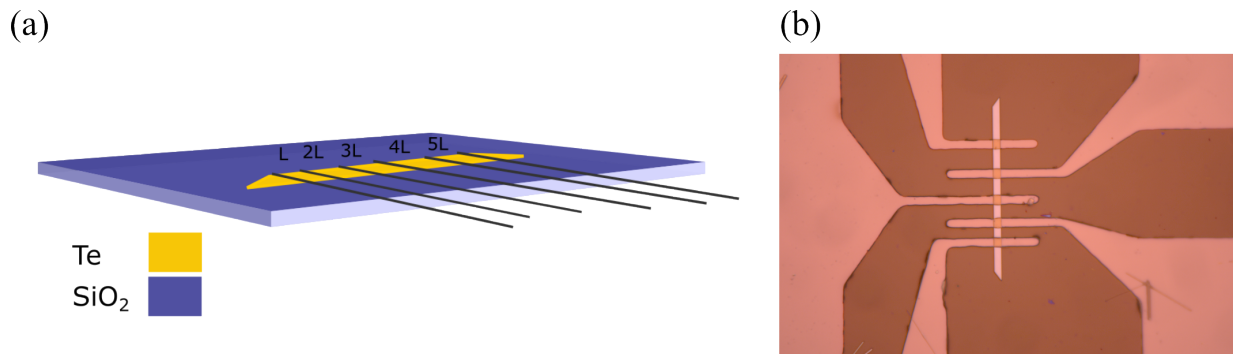


Figure 5.8: (a) Schematic of transfer length geometry (b) Optical image of a transfer length pattern made on tellurene flake

The total resistance between various leads is measured. In this method, the total resistance between any two leads is approximated to be the sum of contact resistance at both

contacts and the sheet resistance of the channel.

$$R_T = 2R_C + L\rho_s \quad (5.2)$$

where R_T is the total resistance between any two leads, R_C is the contact resistance, L is the length of the channel and ρ_s is the resistivity of the material. However, to normalize the values, we use a modified equation:

$$R_T(A_{cross}) = 2R_C(A_{cross}) + L\rho_s(A_{cross}) \quad (5.3)$$

where A_{cross} is the area of cross-section, which can be obtained by the product of width of the channel and the height of the channel (for few layers thick material). It is important to note that this equation works only when the two terms on the right hand side are comparable. Because, if $R_C \gg L\rho_s$, then the equation becomes $R_T = 2R_C$. Hence, the measurement would have majority contribution from contact resistance only.

Several strategies can be used to reduce contact resistance to improve the device performance. In this study we used the choice of contact metal to improve the device performance. From our initial measurements, we decided to analyse Pt, Pd and Ni contacts. Multiple sets of devices for each contact material was studied. Fig.5.9a shows the IV characteristics for various length and the TLM characteristics for Pt contacts. The TLM curves show a very good linear fit. Four devices were measured and the average contact resistance was calculated to be $144 \Omega\mu m^2$. The transfer length was estimated as $1 \mu m$. These results show that Pt is an extremely good contact material for tellurene.

Similarly, TLM measurements were obtained for Pd. Fig.5.9b shows the IV characteristics for various length and the TLM characteristics for Pd contacts. Three devices were measured and the average contact resistance was calculated to be $194 \Omega\mu m^2$. The transfer length was estimated as $1.5 \mu m$. These results show that Pd is also an extremely good contact material for tellurene, but not as good as Pt.

Similar measurements were done for Ni. Fig.5.9c shows the IV characteristics for various length and the TLM characteristics for Ni contacts. Seven devices were measured and the average contact resistance was calculated to be $384 \Omega\mu m^2$. The transfer length was estimated as $1 \mu m$. These results show that Ni is a good contact material for tellurene, but not as good as Pt or Pd.

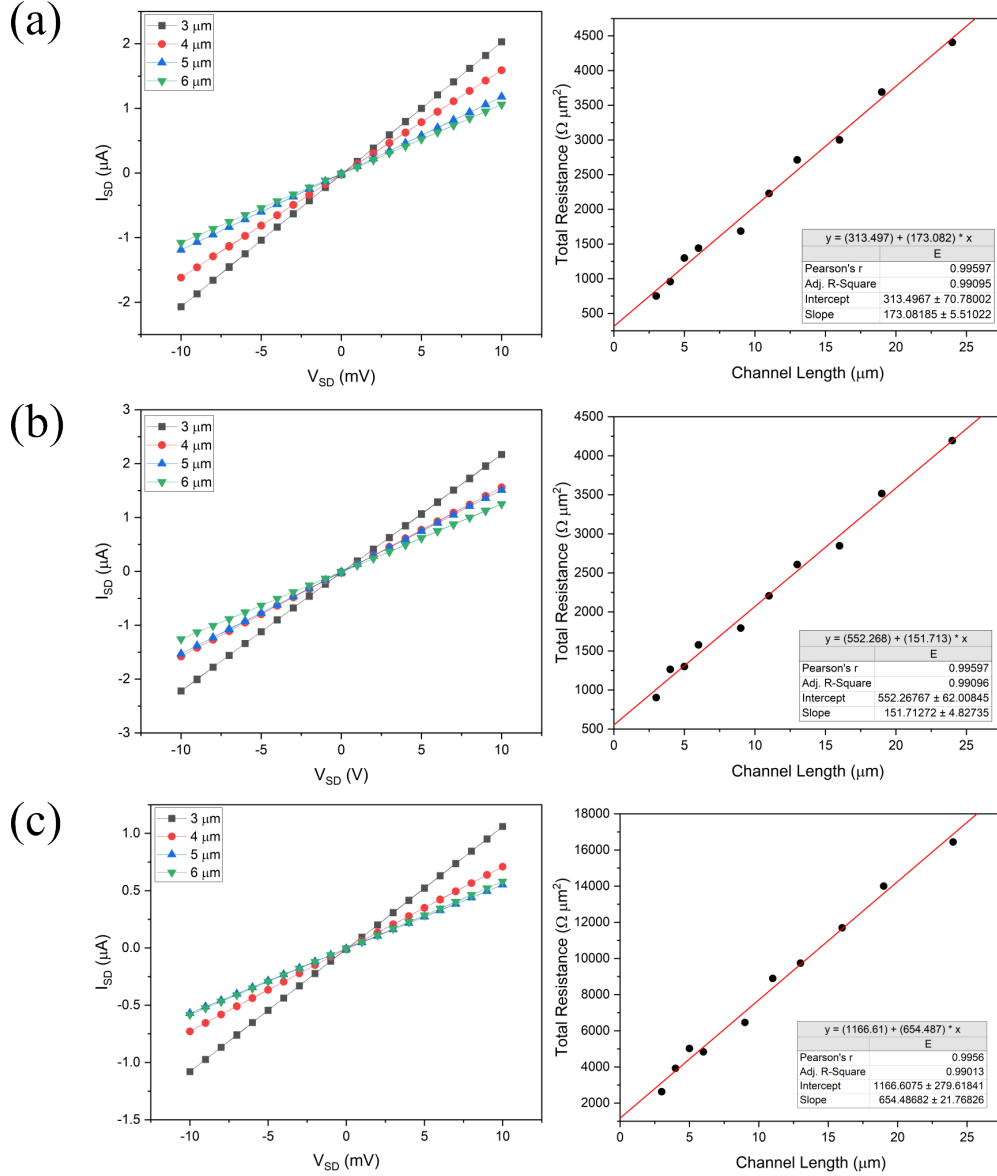


Figure 5.9: I_{SD} vs V_{SD} characteristics for varying channel length and Total resistance vs channel length fit (TLM) for (a) Pt contact (b) Pd contact (c) Ni contact (d) current annealed Au contact

Of the three contact materials tested, Pt had the least contact resistance followed by Pd and then by Ni. However, in literature, Pd and Ni are the commonly used contact material for Tellurene. Our study reveals that Pt has an edge over Pd and Ni as contact material to tellurene.

In addition to the above materials, gold and graphene contacts were also studied. A

transfer length pattern was pre-patterned on a bare SiO₂/Si substrate with 5nm of Cr as the adhesive layer and 30nm of Au as the capping top layer and tellurene flake was transferred on top of it using a dry transfer technique. Initial results obtained showed non-linear IV characteristics. Current annealing was performed by passing pulses of 4V and - 4V repeatedly untill the performance bettered. The IV characteristics before and after current annealing is shown in fig.5.10a The IV characteristics and transfer length curves for gold contact are shown in fig.5.10b and fig.5.10c respectively. The contact resistance was calculated to be $276 \Omega \mu m^2$. The transfer length was estimated as $1.8 \mu m$. These results show that Au is not a good contact material for tellurene.

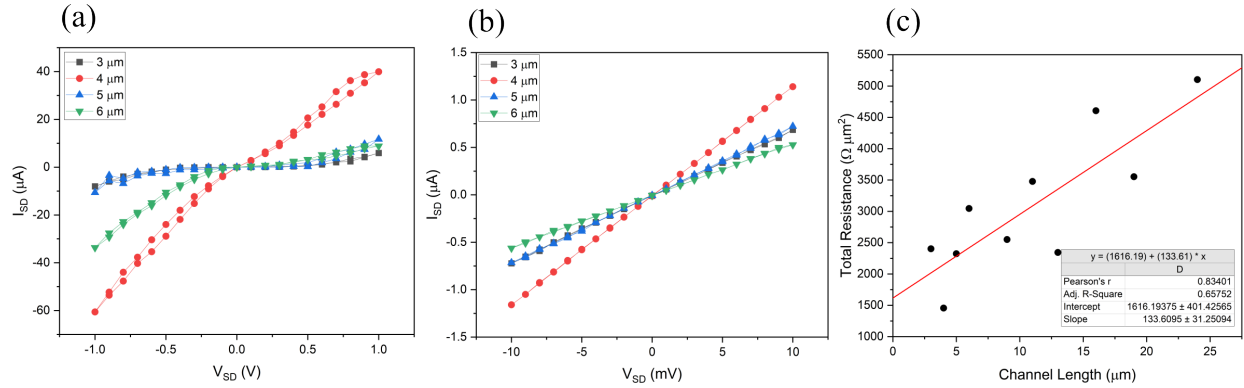


Figure 5.10: (a) I_{SD} vs V_{SD} characteristics for varying channel length in Au contacted TLM device before current annealing (b) I_{SD} vs V_{SD} characteristics for varying channel length in Au contacted TLM device after current annealing (c) Total resistance vs channel length fit (TLM) for Au contact

5.5 Contact induced metallization

Contact induced metallization is a novel observation with huge implication for 2D materials and electronic device engineering. We, for the first time, observed this effect in our research. This entails a change in electronics properties of tellurene upon contact with metal electrodes. There have been few computational reports that suggest contact induced metallization in tellurene with contact metals like Pt, Pd and Ni [20, 27, 28].

From the calculated contact resistance data, we were able to observe extremely low contact resistance for Pt and Pd. This drastic reduction in contact resistance could be indicative of the metallization process. This sheds light on tellurene's novel property and could be helpful for its application in electronic devices. In order to further explore this

phenomenon, temperature dependent measurements were performed. The same devices with transfer length patterns used to extract contact resistance were used for this study. The pads of the devices were extended by a second step of lithography and deposited with 5 nm of Cr and 30 nm of Au to ease the process of wirebonding. Wedge bonding with gold wire was done using a Hybond model 626 system.

In this study, we observed the resistance as a function of temperature. Janis Closed Cycle Helium Cryostat was used to attain low temperature. LakeShore Model 335 was used to control the temperature. Keithley 2450 Source meter was used to do all the electrical measurements.

For Ni contacts, we observed that for 3 μm channel length the resistance decreases with increasing temperature from 10 K to 300 K as shown in fig. 5.11. We observe a semiconducting behaviour where the resistance decreases with increasing temperature. This result was similar to what could be expected. However, the case is complex for Pt and Pd contacts.

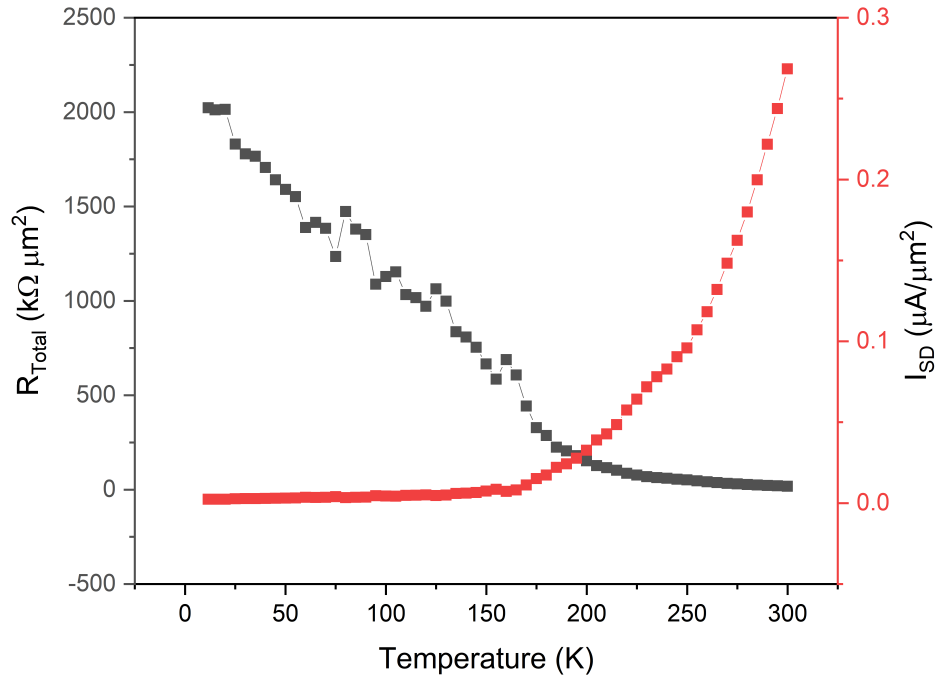


Figure 5.11: Graph of total resistance and I_{SD} as a function of temperature for Ni contacted tellurene device with 3 μm channel length

For Pt contact, we observed a different and more complex behaviour. For 3 μm channel length, the resistance increases with increasing temperature from 10 K to 300 K as shown in fig.5.12a However, for 5 μm channel length, when the temperature is increased from 10

K to 100 K the resistance decreased but increased as the temperature is further increased from to 300 K as shown in fig.5.12b

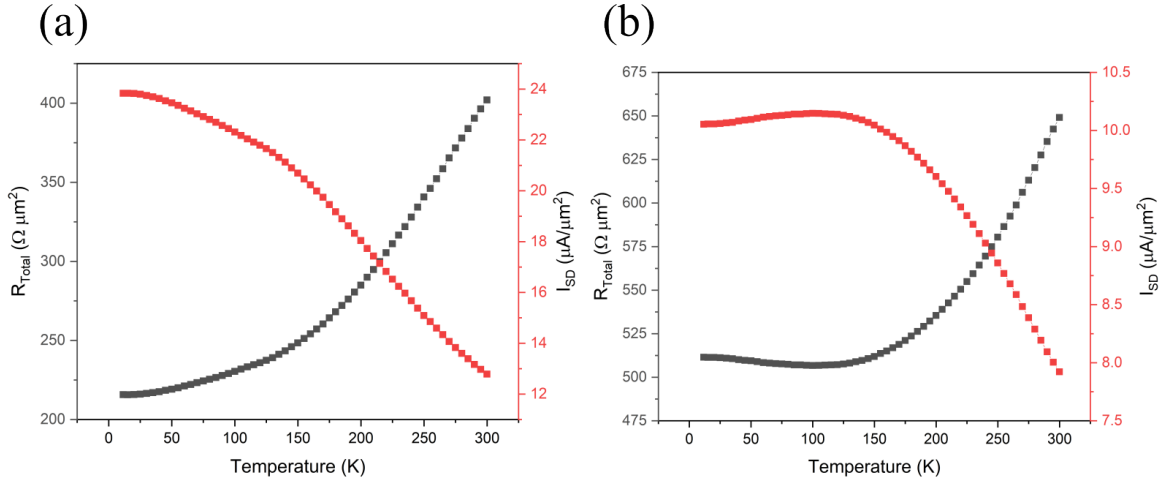


Figure 5.12: Graph of total resistance and I_{SD} as a function of temperature for Pt contacted tellurene device with (a) $3\mu\text{m}$ channel length (b) $5\mu\text{m}$ channel length

A similar but more pronounced effect was observed in for Pd contact. For $3\mu\text{m}$ channel length, the resistance increases monotonically from 10 K to 300 K as shown in fig.5.13a However, for $5\mu\text{m}$ channel length, the resistance shows a non-monotonic behaviour, decreasing from 10 K to 150 K and then increasing from 150 K to 300 K as shown in fig.5.13b

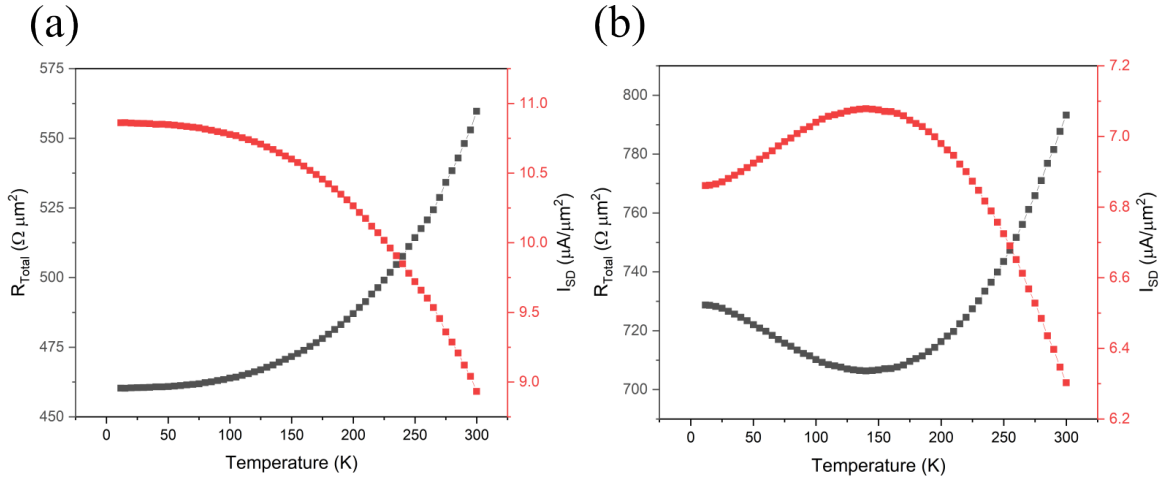


Figure 5.13: Graph of total resistance and I_{SD} as a function of temperature for Pd contacted tellurene device with (a) $3\mu\text{m}$ channel length (b) $5\mu\text{m}$ channel length

This non-monotonic behaviour of R-T could be attributed to a competing behaviour be-

tween the change in resistance of the metallized region of the channel and the change in resistance of the semiconducting region of the channel. We know that a metal has positive temperature coefficient of resistance while a semiconductor has a negative temperature coefficient. In this system, part of the channel is metallic while the other part is semiconducting. Our system can be approximately modelled as two resistors in series R_{metal} and R_{semi} . The total resistance is determined by the sum of resistance of each part ($R_{metal} + R_{semi}$). As the temperature increases, the resistance of metallic part increases while that of the semiconducting part decreases leading to a competing model. At lower temperatures, we hypothesise that the decrease in resistance of the semiconducting part ($|\Delta R_{semi}|$) is larger than the increase in resistance ($|\Delta R_{metal}|$) of the metallic part leading to a decreasing behaviour. As the temperature crosses the transition point, the change in the decrease in resistance of the semiconducting part ($|\Delta R_{semi}|$) is smaller than the increase in resistance ($|\Delta R_{metal}|$) of the metallic part leading to an increasing behaviour.

$$T < T_c \rightarrow |\Delta R_{semi}| > |\Delta R_{metal}| \quad (5.4)$$

$$T > T_c \rightarrow |\Delta R_{semi}| < |\Delta R_{metal}| \quad (5.5)$$

The resistance R_{semi} and R_{metal} can be written as ($\rho_{semi}L_{semi}$) and ($\rho_{metal}L_{metal}$) respectively. The parameter L_{metal} can be assumed to be constant irrespective of the channel length. However, L_{semi} increases with increasing channel length. The change in resistances with temperature can also be written as:

$$\Delta R_{semi} = L_{semi}\Delta\rho_{semi} \quad (5.6)$$

$$\Delta R_{metal} = L_{metal}\Delta\rho_{metal} \quad (5.7)$$

When the channel length was increased from $3\ \mu m$, to $5\ \mu m$, the length of the semiconducting part would also have increased i.e. $L_{semi-3\mu m} < L_{semi-5\mu m}$ but the length of the metallic part would have remained same ($L_{metal-3\mu m} = L_{metal-5\mu m}$). This could be used to explain why a transition from semiconductor dominated transport to metal dominated transport was observed in $5\ \mu m$ channel but not in $3\ \mu m$ channel.

Chapter 6

Optoelectronic Characterization

2D materials are well known for their unique optoelectronic properties. They exhibit various phenomena such as photoluminescence, photoconductivity, photodetection, etc. One of the most important optoelectronic property is photocurrent. Photocurrent refers to the generation of electron-hole pair by absorbing the incident photons. When light of sufficient energy is incident, the carriers are excited across the bandgap leading to the creation of electron-hole pairs.

Photocurrent can provide invaluable insight into the optoelectronic behaviour of the material. In this study, we did a comprehensive investigation of the optoelectronic properties of tellurene with focus on photocurrent. We studied various properties such as photocurrent, spatially resolved photocurrent, time-resolved photocurrent, influence of different contact materials on photocurrent, etc. We have observed the polarization dependent reflectance of tellurene flakes and also studied the polarization dependent photocurrent behaviour using a home-built setup. Our results show that tellurene has a very high responsivity and has high potential for usage as an ultra-broadband detector.

Through these measurements, we gained valuable insights into the optoelectronic properties of tellurene. Our results have added to the understanding of tellurene and increased its potential to be integrated into modern optoelectronic devices.

6.1 Photoresponse

Photoresponse is defined as the ability of a materials to generate electrical signal as a response to incident light. One of the key aspect of the same is generation of photocurrent. Photocurrent is generated when the absorbed photons excite charge carriers across the

bandgap and contribute to the flow of current. It is essential to study the photocurrent of tellurene to enhance the device performance.

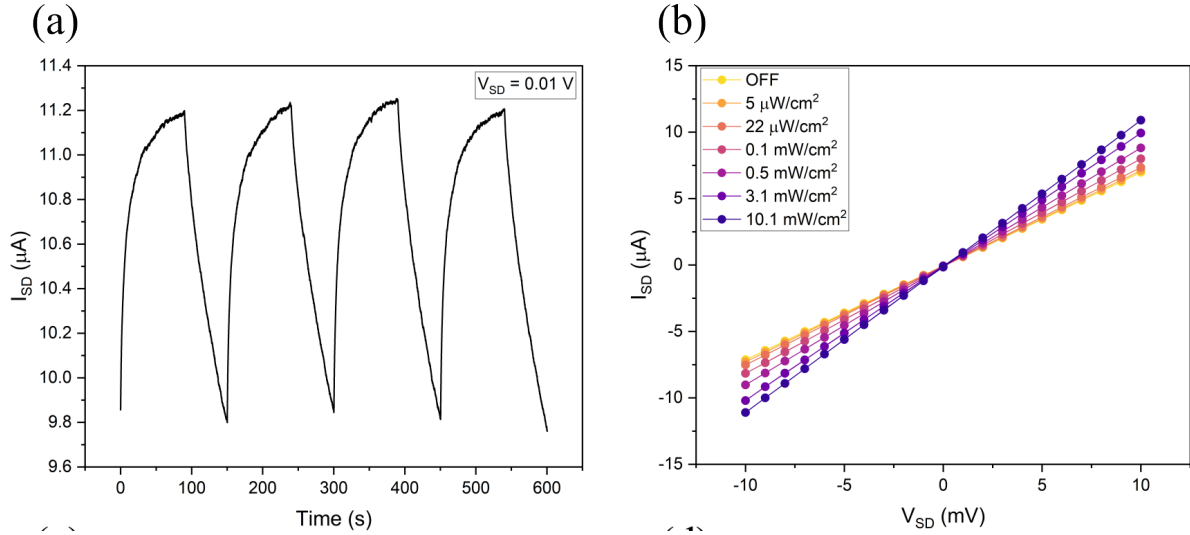


Figure 6.1: (a) Photoresponse of tellurene flake with Pt contacts under illumination with 365nm wavelength LED (b) IV characteristics of tellurene under varying intensity of illumination

One of the common techniques to measure the photoresponse in terms of photocurrent is to study the power dependence of photocurrent. Responsivity, defined as the ratio of generated photocurrent to the power of incident light, is a key parameter to analyse the efficiency of a material in converting photons to electric current. In this study we observed the photocurrent of Tellurene with Pt electrodes. A 2-probe device with Pt electrode was fabricated with $4\ \mu\text{m}$ channel length. The photocurrent was measured in a home-built electrical probe station with keithley 2636B. LED of 365 nm light was used to illuminate the sample.

Tellurene having a small band-gap of 0.38 eV is expected to work as a broadband detector working from the mid-IR to UV range [10, 13, 14]. We used near UV LED to excite the charges and observe the photoresponse. While photoresponse can vary drastically with the wavelength of light used, it has already been shown in the literature that tellurene has a good responsivity in IR and visible range.

Fig.6.1a shows the photoresponse of Pt contacted tellurene flake, while fig.6.1b shows a graph of current vs bias applied at varying light intensities. Zero photocurrent at zero bias implies the absence of self-bias in these flakes. The intensity of incident light was varied using a series resistor box. Fig.6.2 shows the variation in photocurrent and responsivity with

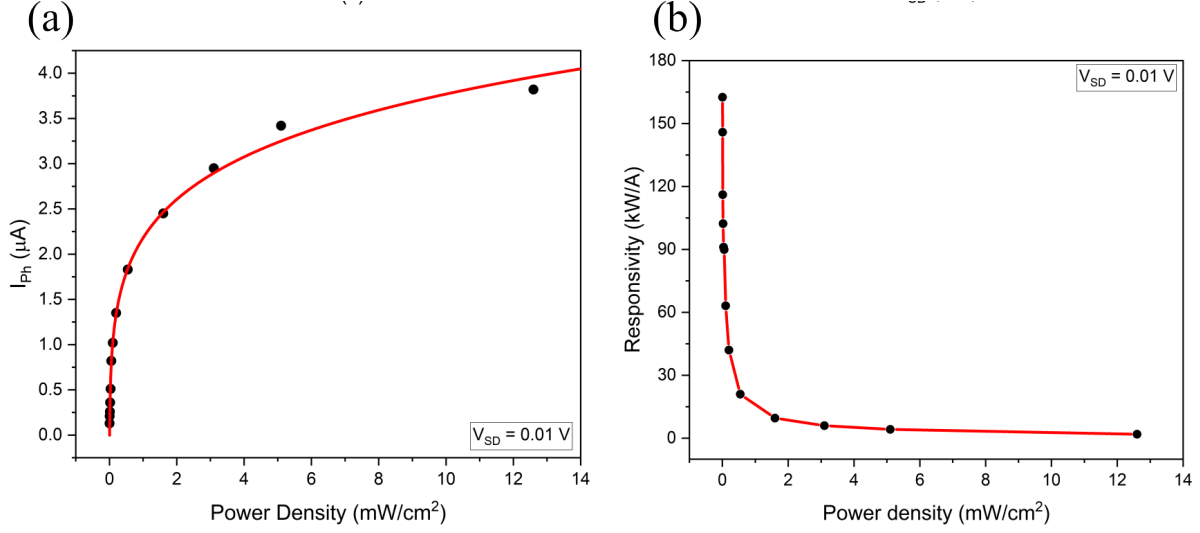


Figure 6.2: (a) Photocurrent as a function of power density of tellurene devices with Pt contacts under illumination with 365nm wavelength LED (b) Responsivity as a function of power density of tellurene devices with Pt contacts under illumination with 365nm wavelength LED

varying power density.

Responsivity can be calculated from photocurrent using the formula:

$$R = \frac{I_{ph}}{P \times A} \quad (6.1)$$

where, I_{ph} is the photocurrent, P is the power density and A is the area of illumination. The responsivity was calculated to be around $1.6 \times 10^5 A/W$

6.2 Time resolved photocurrent

Time resolved photocurrent measurement offers a way to study the dynamics of the carrier generation, transport and recombination in optoelectronic materials. Time resolved photocurrent can be used to study the response of a material to pulses of light. These measurements provide critical insight into the potential of a material to be integrated into an optoelectronic device such as photodetectors. In this study, we observed the time-resolved photocurrent behaviour of tellurene using devices with different contact materials such as Pt, Pd and Ni with 405 nm Laser. The Laser was pulsed on for 10 seconds and kept off for 10 seconds. The rise and fall time of the photocurrent response was measured for different contact materials to understand the generation, transport and recombination of charges in

tellurene devices. Fig.6.3 shows the time resolved photocurrent response for Pt, Pd and Ni respectively.

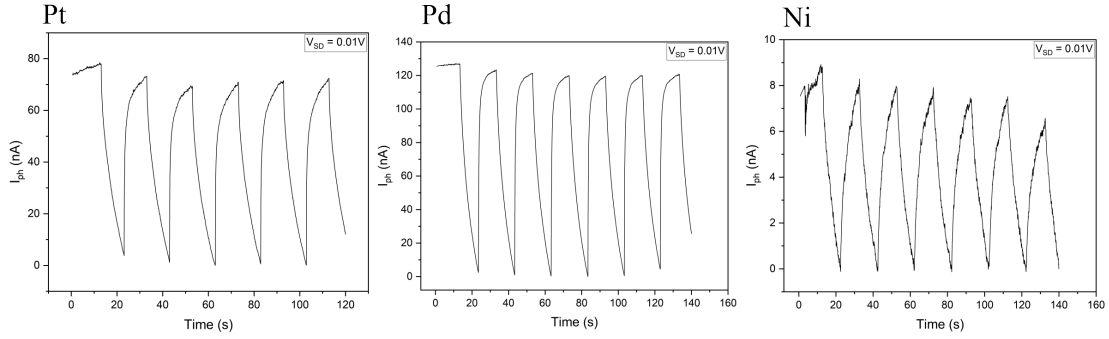


Figure 6.3: Photoresponse of tellurene flake with different contacts under illumination with 405nm wavelength LED

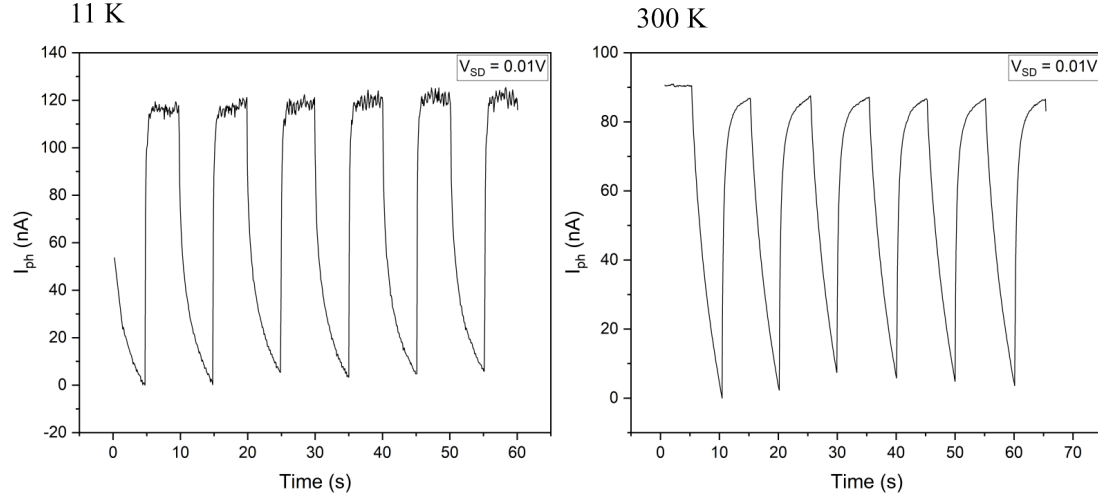


Figure 6.4: Photoresponse of tellurene flake with Pd contact under illumination with 405nm wavelength LED at 11K and 300K

Rise time is defined as the time required to move from 10% to 90% of its final value. While fall time is the time required to move from 90% to 10% of its maximum value. The rise and fall time for these devices were found to be:

Contact Material	Rise time (s)	Fall time (s)
Pt	2.9	7.7
Pd	1.7	9.5
Ni	9.9	7.2

The rise time was found to be smallest for Pd, indicating it to be the best contact material for optoelectronic application of tellurene, followed by Pt and Ni. Ni shows very slow response with persistent photocurrent. However, the fall time seemed to be high for all three materials. Furthermore, such time-resolved photocurrent measurement was also done for device with Pd contact at 11 K. Fig. 6.4 shows the photoresponse of Pd contact at 11K and 300K. We observed that the rise time and fall time improved to 0.35 s and 2.9 s respectively at 11 K as compared to 1.4 s and 3.7 s at 300 K. These findings highlight the importance of contacts and temperature in optimizing the optoelectronic properties of tellurene.

6.3 Spatially resolved photocurrent

Spatially resolved photocurrent is used to map the spatial contribution of a material to the generation of photocurrent. Conventional photocurrent measurement gives an average response of the entire sample. Whereas, spatially resolved photocurrent allows for the study of local variation in photocurrent. By spatially mapping photocurrent distribution, we can identify the region of high and low efficiency. It can also be used to understand the underlying mechanism of photocurrent generation. In this study we used a home-built spatially resolved photocurrent setup. A 405 nm Laser was used for illumination. The spot size used was around 2 μm . Keithley 2450 Source meter was used for doing electrical measurements.

In this study, we measured the spatially resolved photocurrent measurement on tellurene based devices with different contact materials like Pt, Pd and Ni. Our aim was to understand the mechanism of photocurrent generation. Changing photoresponse with different contact material might be an indication of Schottky barrier lowering induced photocurrent. To understand whether the photocurrent generation occurs in the channel or at the contacts, light was incident on the interface and channel separately and the corresponding photocurrent was studied. Fig.6.5 shows an optical image of the incident laser spot on the desired area.

We observed that the overall photocurrent generated changed for different contact materials. Fig.6.6 shows the photocurrent measured for different contacts when light is incident on different regions. From the graph, we observe that maximum photocurrent is generated when light is incident on the channel. When light is incident on the contact-channel interface, the photocurrent generated is less than or equal to that when the light is incident on the channel. This could mean that the generation of photocurrent happens primarily in the tellurene bulk and not because of the contacts.

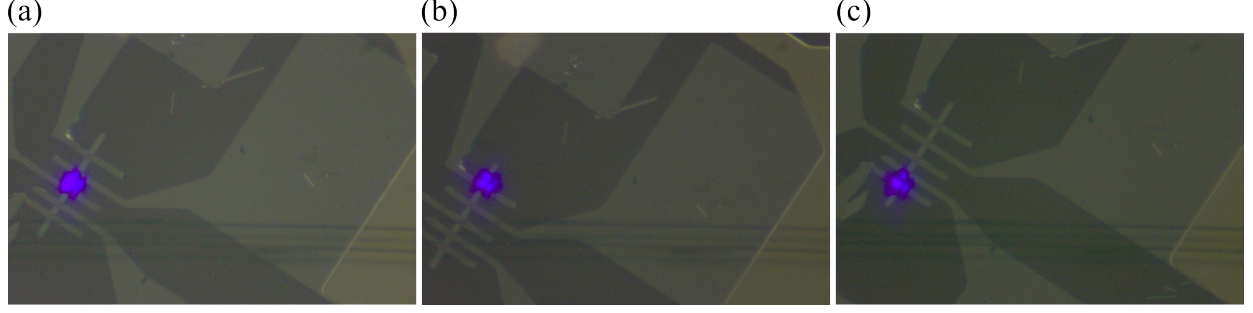


Figure 6.5: Optical image showing spatial illumination of (a)Bulk channel (b)Lead-1 (c)Lead-2

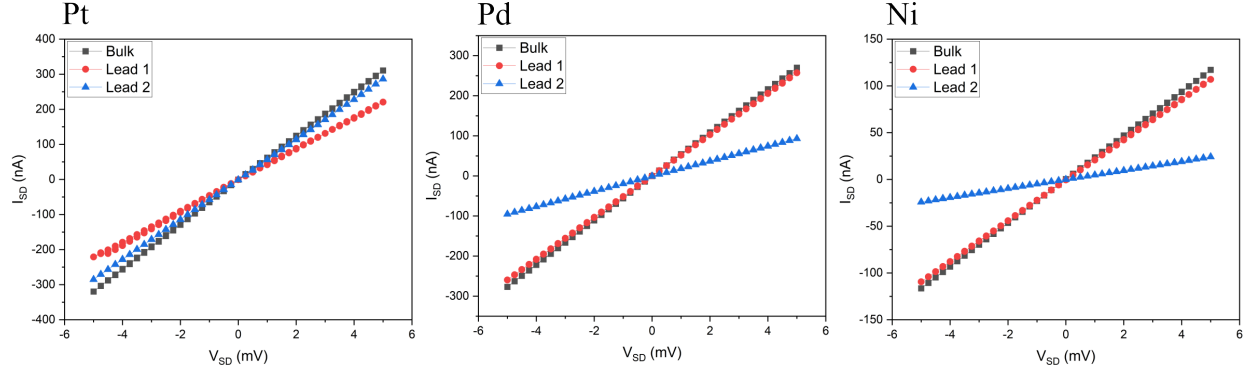


Figure 6.6: Spatial photocurrent of tellurene devices with different contacts

Hence, overall through this study we provide valuable insights into the optoelectronic properties of tellurene and pave way for its optimization to be integrated into modern electronics.

6.4 Polarization dependence

Certain 2D materials have different response when incident with light with certain polarization angle. Tellurene, due to its one dimensional chain like structure, exhibits strong polarization dependence [13, 14]. To demonstrate the potential application of tellurene in polarization sensitive photonic and optoelectronic devices, we performed polarization dependent imaging.

In this experiment, we captured the images of tellurene flake using a polarized optical microscope. The change in colour and contrast of the flakes with polarization angle was observed. To visualize this, we placed a linear polarizer in front of the light source and rotated it by different angles. We observed that the colour and contrast of the flakes changed with

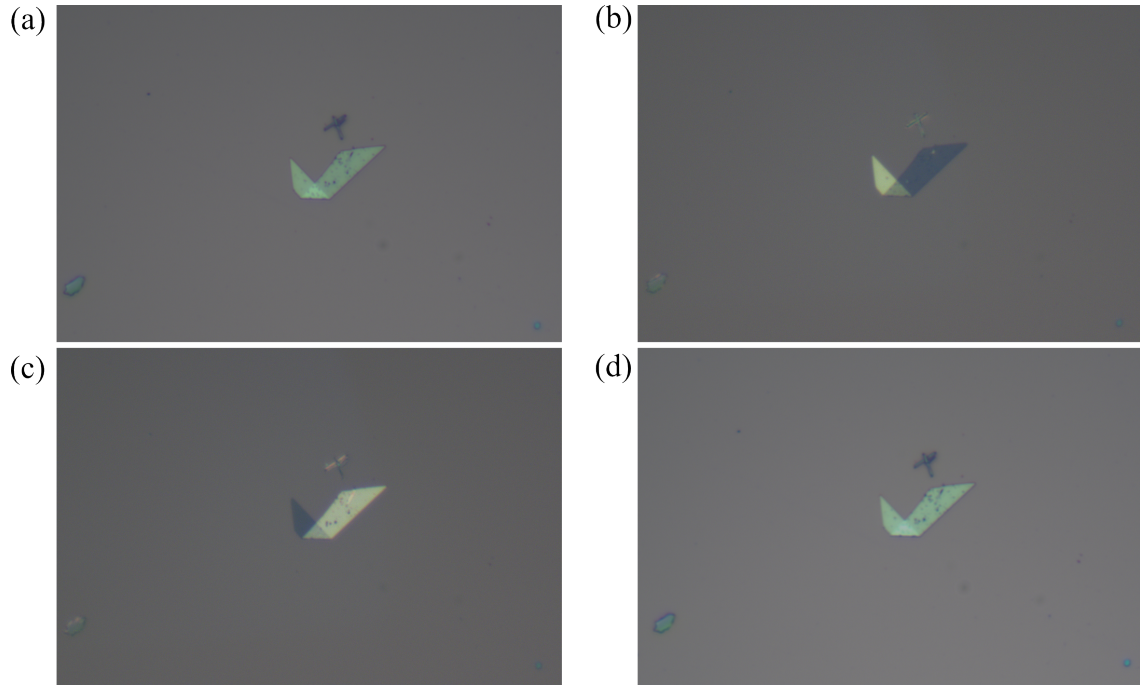


Figure 6.7: Optical image of tellurene flake using polarized light at (a) 0° (b) 80° (c) 110° (d) 180°

change in polarization angle of the incident light. Fig.6.7 shows the polarization dependent optical image of a folded tellurene flake. This result reflects the anisotropic optical property of tellurene

Chapter 7

Conclusion and future scope

This work commenced with the synthesis of high quality tellurene. Through careful control of growth parameters, we achieved a reproducible synthesis with desirable morphology of tellurene. Further, we did extensive structural characterizations utilizing techniques such as AFM, SEM, Raman spectroscopy, etc. to get insights about the crystallinity and purity of the synthesized samples.

The culmination of this work on the electrical and optoelectronic properties of tellurene offers valuable insights into its potential applications. This study has provided indepth insights into conductivity, carrier mobility, and FET characteristics of tellurene. We have also critically studied the effect of various contact materials with tellurene. We have quantified the contact resistance of Pt, Pd and Ni with these flakes and explored the possibility of Au and graphene contacts. Pt and Pd were concluded to be the contact materials with least contact resistance.

This study included the observation of contact induced metallization of tellurene. Temperature dependent studies were performed to understand the phenomena in detail. These could help in mitigating the parasitic effects and increasing the device efficacy. Overall, we have significantly contributed to lay a foundation for the design and engineering of tellurene based electronic devices with tailored features.

In parallel, we also explored the optoelectronic properties of tellurene. A systematic study of the material's photoresponse, time resolved photocurrent, and spatially resolved photocurrent shed light on the mechanism of carrier generation and transport. The synthesized material had very high responsivity and can be effectively used for photodetection. We also imaged the flakes with polarized light to understand its polarization dependence. Extensive study of photoresponse under various conditions have added to the foundation to

integrate tellurene into modern optoelectronic devices.

In future, we observe that tellurene holds immense promise and potential. Continued efforts are required to understand the material's electronic and optoelectronic properties. It would be very interesting and essential to study carrier dynamics, band structure engineering and defect engineering of tellurene for device application. It would also be immensely important to work further on the thickness control of the synthesized flakes in hydrothermal technique. Additionally the exploration of hybrid structures and heterostructures involving tellurene and other 2D materials holds great potential. We fabricated a device with tellurene as contacts and MoS₂ as the channel.

We observed that this heterostructure has a very low rise and fall time as compared to both tellurene and MoS₂. There are some reports of charge transfer between tellurene and MoS₂ as well. These heterostructures can have huge potential for application in modern electronics. Further study about the stability and reliability of tellurene under real world operating conditions would be essential for transition from laboratory scale to industry scale. We plan to further study the contact induced metallization phenomena to understand the cause and effect of the same. We plan to do KPFM on the devices to get an idea of the length of channel that undergoes metallization. Further we can also check whether the metallization is reversible or not. An interdisciplinary and holistic approach encompassing the synthesis, device fabrication, and theoretical modelling is encouraged to harness the full potential of tellurene to address the pressing challenges in electronics, optoelectronics, photonics, etc.

Bibliography

- [1] Novoselov, K. S. et al. Electric Field Effect in Atomically Thin Carbon Films. *Science* 306, 666–669 (2004).
- [2] Novoselov, K. S., Mishchenko, A., Carvalho, A. & Castro Neto, A. H. 2D materials and van der Waals heterostructures. *Science* 353, (2016).
- [3] Geim, A. K. & Grigorieva, I. V. Van der Waals heterostructures. *Nature* 499, 419–425 (2013).
- [4] Hu, Z. et al. Two-dimensional transition metal dichalcogenides: interface and defect engineering. *Chem. Soc. Rev.* 47, 3100–3128 (2018).
- [5] Murali, G. et al. A review on MXenes: new-generation 2D materials for supercapacitors. *Sustainable Energy Fuels* 5, 5672–5693 (2021).
- [6] Wang, T. et al. Xenos as an Emerging 2D Monoelemental Family: Fundamental Electrochemistry and Energy Applications. *Advanced Functional Materials* 30, 2002885 (2020).
- [7] Wang, Y. et al. Field-effect transistors made from solution-grown two-dimensional tellurene. *Nat Electron* 1, 228–236 (2018).
- [8] Yoon, J. et al. Environmentally Stable and Reconfigurable Ultralow-Power Two-Dimensional Tellurene Synaptic Transistor for Neuromorphic Edge Computing. *ACS Appl. Mater. Interfaces* 15, 18463–18472 (2023).
- [9] Zhu, Z. et al. Multivalency-Driven Formation of Te-Based Monolayer Materials: A Combined First-Principles and Experimental study. *Phys. Rev. Lett.* 119, 106101 (2017).
- [10] Amani, M. et al. Solution-Synthesized High-Mobility Tellurium Nanoflakes for Short-Wave Infrared Photodetectors. *ACS Nano* 12, 7253–7263 (2018).
- [11] Sharma, S., Singh, N. & Schwingenschlögl, U. Two-Dimensional Tellurene as Excellent Thermoelectric Material. *ACS Appl. Energy Mater.* 1, 1950–1954 (2018).
- [12] Rao, G. et al. Robust Piezoelectricity with Spontaneous Polarization in Monolayer Tellurene and Multilayer Tellurium Film at Room Temperature for Reliable Memory. *Advanced Materials* 34, 2204697 (2022).

- [13] Wu, W., Qiu, G., Wang, Y., Wang, R. & Ye, P. Tellurene: its physical properties, scalable nanomanufacturing, and device applications. *Chem. Soc. Rev.* 47, 7203–7212 (2018).
- [14] Shi, Z. et al. Two-Dimensional Tellurium: Progress, Challenges, and Prospects. *Nano-Micro Lett.* 12, 99 (2020).
- [15] . Li, Q. et al. Bilayer Tellurene: A Potential p-Type Channel Material for Sub-10 nm Transistors. *Advanced Theory and Simulations* 4, 2000252 (2021).
- [16] Wang, G., Guan, Y., Wang, Y., Ding, Y. & Yang, L. Direct Laser Irradiation and Modification of 2D Te for Development of Volatile Memristor. *Materials* 16, 738 (2023).
- [17] Kramer, A., Van de Put, M. L., Hinkle, C. L. & Vandenberghe, W. G. Tellurium as a successor of silicon for extremely scaled nanowires: a first-principles study. *npj 2D Mater Appl* 4, 1–8 (2020).
- [18] Zhu, Z. et al. Tellurene-a monolayer of tellurium from first-principles prediction. Preprint at <https://doi.org/10.48550/arXiv.1605.03253> (2016).
- [19] Wu, K., Ma, H., Gao, Y., Hu, W. & Yang, J. Highly-efficient heterojunction solar cells based on two-dimensional tellurene and transition metal dichalcogenides. *J. Mater. Chem. A* 7, 7430–7436 (2019).
- [20] Yan, J. et al. Monolayer tellurene–metal contacts. *J. Mater. Chem. C* 6, 6153–6163 (2018).
- [21] Apte, A. et al. Polytypism in ultrathin tellurium. *2D Mater.* 6, 015013 (2018).
- [22] Zhao, C. et al. Evaporated tellurium thin films for p-type field-effect transistors and circuits. *Nat. Nanotechnol.* 15, 53–58 (2020).
- [23] Wang, Q. et al. Van der Waals Epitaxy and Photoresponse of Hexagonal Tellurium Nanoplates on Flexible Mica Sheets. *ACS Nano* 8, 7497–7505 (2014).
- [24] Xie, Z. et al. Ultrathin 2D Nonlayered Tellurium Nanosheets: Facile Liquid-Phase Exfoliation, Characterization, and Photoresponse with High Performance and Enhanced Stability. *Advanced Functional Materials* 28, 1705833 (2018).
- [25] Yan, B. et al. 2D tellurene/black phosphorus heterojunctions based broadband nonlinear saturable absorber. *Nanophotonics* 9, 2593–2602 (2020).
- [26] Khatun, S., Banerjee, A. & Pal, A. J. Nonlayered tellurene as an elemental 2D topological insulator: experimental evidence from scanning tunneling spectroscopy. *Nanoscale* 11, 3591–3598 (2019).

- [27] Mitra, S., Kesharwani, O. & Mahapatra, S. Ohmic-to-Schottky Conversion in Monolayer Tellurene–Metal Interface via Graphene Insertion. *J. Phys. Chem. C* 125, 12975–12982 (2021).
- [28] Pang, H. et al. Bilayer tellurene–metal interfaces. *J. Semicond.* 40, 062003 (2019).
- [29] Haley, K. L. et al. Heated Assembly and Transfer of Van der Waals Heterostructures with Common Nail Polish. *Nanomanufacturing* 1, 49–56 (2021).