

Exploring Thermoelectric Potential: Seebeck Coefficient Investigations in Bi_2S_3 Thin Films

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

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March, 2024

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Certificate

This is to certify that this dissertation entitled “ Exploring Thermoelectric Potential: Seebeck Coefficient Investigations in Bi_2S_3 Thin Films” 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 Adhiraj Sundar at Indian Institute of Science, Bangalore under the supervision of Dr Abha Misra, Professor, Instrumentation and Applied Physics Department, Indian Institute of Science, Bangalore during the academic year 2023-2024.



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“ Research is what I’m doing when I don’t know what I’m doing.”

— **Wernher von Braun**

This thesis is dedicated to my parents and my sister.

Declaration

I hereby declare that the matter embodied in the report entitled "**Exploring Thermoelectric Potential: Seebeck Coefficient Investigations in Bi_2S_3 Thin Films**", are the results of the work carried out by me at the Instrumentation and Applied Physics Department, Indian Institute of Science, Bangalore, and in affiliation with Indian Institute of Science Education and Research, Pune under the supervision of Dr Abha Misra 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 acknowledgment of collaborative research discussions.



Adhiraj Sundar

20191105

Acknowledgments

I am profoundly grateful for the consistent support and guidance I've received throughout this project. Without the help and encouragement of many individuals, navigating this journey would have been much more difficult.

First and foremost, I am grateful to my supervisor, Dr. Abha Misra, for accepting me as a research student in her lab and for demonstrating unwavering faith in my abilities throughout the entire duration of our collaboration. Our regular meetings, which occurred almost daily, provided a platform to discuss progress and brainstorm ideas. Dr. Misra's availability for these meetings and her willingness to extend support whenever needed were truly invaluable. Her guidance and support really influenced my approach, especially in the early phases of the project when I was developing the plan and direction.

I also extend special thanks to Krishnakumar, a fellow lab member, for his support and guidance throughout the project. He provided invaluable assistance and camaraderie, offering clarity and shaping the project's trajectory during the initial stages. His expertise and training in electrical measurement methods were crucial, and I am truly thankful for his mentorship and friendship. I extend my gratitude to Namrata Harbola, with whom I collaborated closely throughout the research process. Together, we tackled tasks ranging from the exfoliation of flakes to their transfer onto substrates, supporting each other every step of the way. I am especially thankful for her selfless efforts in conducting the e-beam lithography of my devices at CeNSE. I would like to express my appreciation to Rajesh, who recently joined me in this project and provided valuable assistance during the latter stages of our research. I also extend my gratitude to Vinod, whose previous research on this material gave me the support and inspiration for my work. I also wish to thank all other lab members for their support throughout this journey.

I express my gratitude to INSPIRE for providing the fellowship that supported my scientific research endeavors. Additionally, I extend my thanks to the Instrumentation and Applied Physics Department and the CeNSE facilities at IISc for providing the necessary resources for the completion of this thesis.

A special thank you to my friend Haroon, who was a huge help to me when I was in Bangalore. Our late-night AFM microscopy sessions, arranged in his slots, were both productive and enjoyable! I am grateful for the friendships I formed in Bangalore, including those with Sreevani, Avani, Malavika, Chaithra, Marwa, Aslaha, and a few others. These memories will always hold a special place in my heart. Thank you all for the wonderful experiences.

My fascination with 2D materials blossomed during my first semester project at IISER Pune, marking the beginning of my journey in experimental physics. I am thankful for the opportunity to study at this esteemed institute, where I had the privilege of meeting and befriending numerous exceptional individuals. I extend heartfelt gratitude to my batchmates, especially Abhilash, Nived, Athul, Darsan, Salima, Namitha, Amisha, and my seniors and juniors, as well as the Vedikettu family, for their companionship and friendship throughout my time at IISER. I also express my gratitude to Maria for her consistent support and generosity.

Finally, my deepest gratitude goes to my family, especially my parents and my sister, whose unwavering love and support have been the guiding light of my journey. Their belief in me, their encouragement, and their unwavering presence have been the bedrock of my every step. Their sacrifices, their endless encouragement, and their boundless love have shaped me into the person I am today, and for that, I am eternally grateful.

Contributions

Contributor	Contribution
Adhiraj Sundar and Dr. Abha Misra	Conceptualization Ideas
Adhiraj Sundar and Dr. Abha Misra	Methodology
Adhiraj Sundar and Dr. Abha Misra	Validation
Adhiraj Sundar and Rajesh P Achari	Formal Analysis
Adhiraj Sundar, Namrata Harbola and Rajesh P Achari	Investigation
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Adhiraj Sundar	Writing - original draft preparation
Adhiraj Sundar and Dr. Abha Misra	Writing - review and editing
Adhiraj Sundar	Visualization
Dr. Abha Misra	Supervision
Dr. Abha Misra	Funding acquisition

Abstract

In response to escalating global energy demands and environmental concerns, the exploration of efficient and clean energy conversion technologies becomes imperative. Thermoelectric materials emerge as a promising solution, directly transforming waste heat into usable electricity, thus promoting energy harvesting and sustainability. Among these materials, Bismuth sulfide (Bi_2S_3) has gained attention due to its high electrical conductivity and tunable thickness-dependent bandgap.

This research delves into the less-explored domain of in-plane thermoelectric potential in Bi_2S_3 thin films, diverging away from extensively studied bulk forms. Our focus zooms in on the micro and nanoscale thermopower or Seebeck effect of these thin films. Through our custom-built measurement devices, we've uncovered promising thermoelectric properties in Bi_2S_3 thin films at both scales. Our findings highlight their potential as versatile thermoelectric materials, providing valuable insights for future exploration and development in practical energy conversion applications. This research paves the way for a cleaner and more sustainable energy future.

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List of Abbreviations

DUT	Device Under Test	PDMS	Polydimethylsiloxane
EBL	Electron Beam Lithography	PLCC	Plastic Leaded Chip Carriers
FOM	Figure of Merit	TCR	Temperature Coefficient of Resistance
IPA	Isopropyl alcohol	TE	Thermoelectric
MIBK	Methyl isobutyl ketone	TEG	Thermoelectric Generator
PCB	Printed Circuit Board		

Chapter 1

Introduction

1.1 Motivation

The world currently obtains nearly 80% of its energy needs from the remaining limited stocks of oil, gas, and coal—a resource that is running out faster than expected—despite some success in using renewable energy, which accounts for less than 10% of the average global primary power consumption. While global energy demand shows no sign of easing (EI, 2023) (Figure 1.1).

Approximately 70% of the energy obtained from fossil fuels is dissipated as unused heat, either through combustion exhaust emissions or as a result of cooling requirements. There exists an urgent and immediate demand for sustainable solutions aimed at enhancing energy conversion efficiency and effectively recovering wasted heat that would otherwise be lost (U.S. Energy Information Administration (EIA), 2023). The production of useful energy from omnipresent or lost energy is called "energy harvesting" and has gained significant attention in fulfilling world energy requirements. As a result, continued efforts are aimed towards introducing new technologies, with a greater emphasis on improving the conversion efficiency of existing ones.

Among these technologies, thermoelectrics stands out as an attractive and swiftly advancing method for harvesting energy, efficiently transforming waste heat into valuable electric power (Rowe, 2018). Therefore, thermoelectric materials can contribute to both energy con-

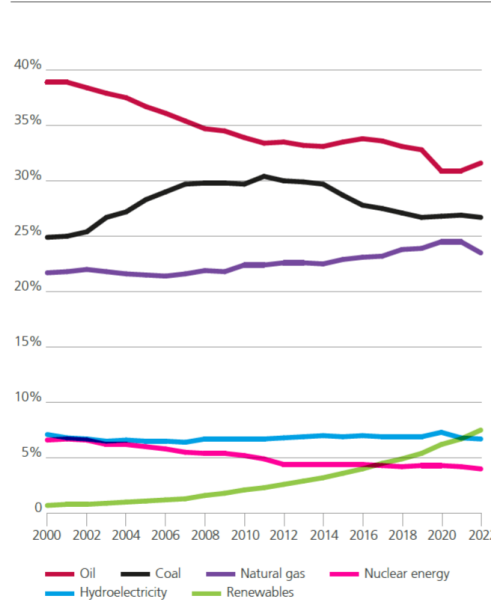


Figure 1.1: Global Primary Energy Consumption: This figure illustrates the distribution of global primary energy consumption from 2000 to 2022. Extracted from (EI, 2023)

servation and primary power generation. The TE energy harvesting technology has various advantages, including its compact design, durability, zero fuel emissions, and noiseless and maintenance-free operation. These properties make TE devices a highly promising alternative to renewable energy (Zhu et al., 2017). They have been implemented or are under development in fields like deep space projects, military, temperature detection and measurement devices, transportation, and, more broadly, satisfying energy conservation and environmental protection needs (Rowe, 2018). The current state-of-the-art TEGs face a significant practical limitation in their relatively low efficiency compared to other electric generators. This efficiency is strongly dependent on the TE performance of the materials. Consequently, TE materials have been confined to niche applications rather than widespread use. Developing high-efficiency thermoelectric materials for waste-heat recovery systems has become increasingly critical. This challenge, if effectively addressed, not only holds the promise of substantial economic benefits but also offers the potential for significant environmental advantages.

This chapter is dedicated to exploring the fundamental principles that are important for understanding ongoing research in thermoelectric materials. In addition, we look at ways to improve thermoelectric efficiency, establishing a comprehensive understanding of the subject.

1.2 Thermoelectricity

As the name suggests, thermoelectricity is the direct solid-state conversion of thermal energy using thermoelectric materials into electrical energy or vice versa. The fundamental principle underlying thermoelectricity is the Seebeck effect, which was initially observed by a German physicist, Thomas Johann Seebeck. It demonstrates the capability of specific materials to produce an electric voltage when subjected to a gradient in temperature. If a circuit is formed by connecting two dissimilar materials and a temperature difference is applied across them, an electric voltage is produced. This voltage arises from the flow of charge carriers, such as electrons or holes, due to the thermal gradient. When these dissimilar metals are assigned p-type and n-type semiconductor legs, the device is known as a thermoelectric generator (TEG). A single TEG consists of a pair of p-type and n-type legs. Later, it was discovered that passing an external electric current in the circuit produces temperature differences across the junctions, known as the Peltier effect, named after the French physicist J. Peltier. The interdependence of these phenomena was recognized by W. Thomson. He indicated the presence of another thermoelectric effect in a homogeneous conductor, now identified as the Thomson effect. This is basically reversible heating or cooling when there is both an electric current flow and a temperature gradient (Goldsmid, 2009). While these effects may appear to be primarily interfacial due to their manifestation at the junctions between dissimilar conductors, they are fundamentally grounded in the bulk properties of the materials employed.

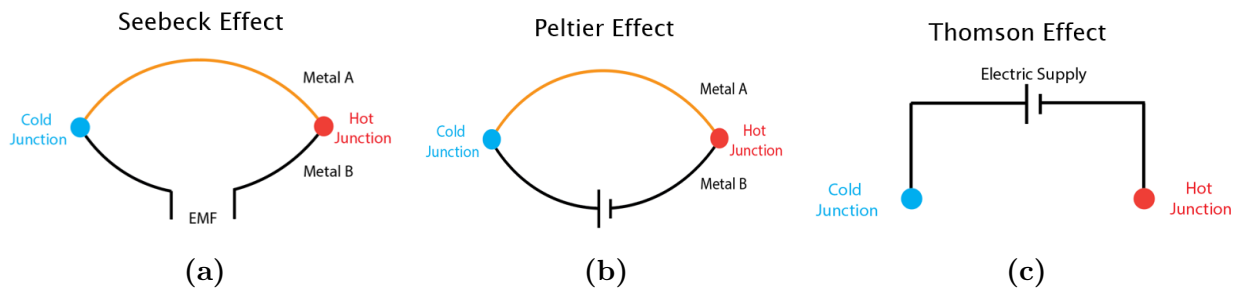


Figure 1.2: Thermoelectric Effects: Basic illustration of a) Seebeck Effect b) Peltier Effect and c) Thomson Effect. (Goldsmid, 2009)

1.2.1 Seebeck Effect

Seebeck effect was initially named "thermomagnetism" by Seebeck as he linked the development of magnetism in metal circuits to the temperature difference generated. Hans Christian Oersted later clarified that the magnetic field resulted from the generated voltage due to the temperature difference, introducing the concept of thermoelectricity, though the phenomenon continued to be known as the Seebeck effect (Seebeck, 1826). The voltage generated is proportional to the temperature gradient, with the constant of proportionality known as the Seebeck coefficient (S) or thermopower or thermal EMF coefficient. Therefore, the Seebeck coefficient can be defined as,

$$S = \frac{\Delta V}{\Delta T} , \tag{1.1}$$

where ΔV is the potential difference generated across the junctions, and ΔT is the magnitude of the temperature difference applied between the junctions. It has the units in $\mu\text{V}/\text{K}$. Here, the directional nature of the generated ΔV depends on the direction of the temperature gradient and the constituent material's intrinsic properties. As a convention, S is considered positive when the thermoelectric current flows from the hot end to the cold end in the conductor.

The generation of a potential difference arises from fluctuations in charge distribution within a conductor experiencing a temperature gradient. In a p-type semiconductor, initially electrically neutral with a uniform charge distribution, applying heat creates a temperature difference. This causes holes, the majority of charge carriers, to gain more kinetic energy at the hotter end, leading to their diffusion towards the colder end. This establishes a non-uniform charge distribution and forms an inner electric field, resulting in a reverse drift charge current and a steady voltage upon reaching dynamic equilibrium. This phenomenon applies to both p-type and n-type semiconductors, with the Seebeck voltage being positive for p-type materials and negative for n-type ones. In ambipolar semiconductors, factors like carrier concentrations and band characteristics influence the Seebeck coefficient's sign, not solely relying on carriers being electrons or holes. Thermoelectric generators (TEGs) utilize this effect to convert thermal energy into electrical energy (Chen et al., 2023) (Chen et al., 2020).

1.2.2 Peltier Effect

Imagine reversing the Seebeck effect. That's essentially the Peltier effect! Instead of a temperature difference creating a voltage, the Peltier effect uses an electric current to drive heat flow. Apart from Joule heat, additional heat is generated and absorbed at the junctions of the conductor when an electric current flows through it. In a conductor, the rate of heat absorption or emission (Q) is directly proportional to the applied electric current (I), represented as:

$$\frac{dQ}{dt} = \pi I, \quad (1.2)$$

where π is the differential Peltier coefficient of the material with the unit of V . The Peltier effect drives cooling in thermoelectric refrigerators (Richmond, 1966), and a typical TEG/refrigerator consists of a p-n leg unit arranged electrically series and thermally parallel connections with conductive electrodes (Figure 1.3). When electrons flow from a metal to a p-type material, they fill holes, absorbing heat in the process. This results in a cooling effect and thus a positive π and vice versa for an n-type semiconductor. Thus, the Seebeck coefficient and Peltier coefficient have a direct correlation, expressed as $\pi = TS$, which has been realized by Kelvin.

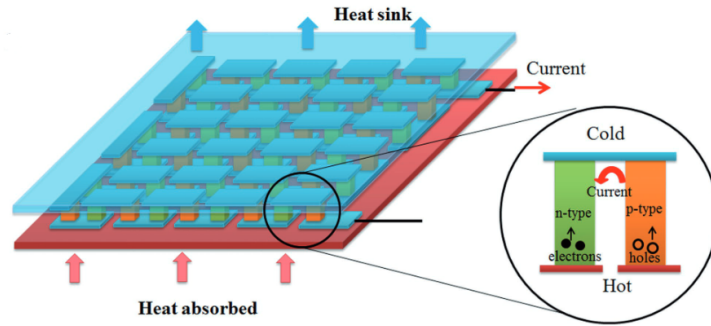


Figure 1.3: Thermoelectric Generator (TEG): Figure illustrates the basic structure of a Thermoelectric Generator (TEG) and its fundamental unit comprising p-type and n-type legs. (Yang et al., 2017)

1.2.3 Thomson Effect

Kelvin proposed a third thermoelectric effect known as the Thomson effect, which occurs when an electric current I flows through a uniform conductor with a temperature gradient, resulting in reversible heat absorption or release alongside Joule heat. Thus, the rate of heat transfer is given as,

$$\frac{dQ}{dt} = \beta \Delta T I, \quad (1.3)$$

where β is the Thomson coefficient (V/K) (Thomson, 1857). Compared to the other two thermoelectric effects, this effect has an insignificant role in thermoelectric conversion.

1.3 Thermoelectric efficiency

Similar to a heat engine, the efficiency of a thermoelectric energy conversion system, denoted as (η) , is a crucial performance metric. It quantifies the ratio of useful electrical power output to the total heat input.

$$\eta = \frac{P}{Q}, \quad (1.4)$$

where P is the load power output and Q is the heat supplied at one end of the thermoelectric conductor. Here, a dimensionless parameter is defined to quantify the efficiency called $Z\bar{T}$ where Z is called the *Figure of Merit* (FOM) as (Minnich et al., 2009)

$$Z = \frac{S^2 \sigma}{\kappa}, \quad (1.5)$$

which shows Z is dependent on the material's properties, σ , electrical conductivity, and κ , the total thermal conductivity, which comprises both lattice (κ_l) and electronic distribution (κ_e). These quantities are inherently dependent on the length and area of the material. Using the figure of merit, the thermoelectric efficiency is given as (Lan et al., 2010):

$$\eta = \left(1 - \frac{T_c}{T_h}\right) \frac{\sqrt{1 + Z\bar{T}} - 1}{\sqrt{1 + Z\bar{T}} + T_c/T_h}, \quad \text{where } \bar{T} = (T_h + T_c)/2 \quad (1.6)$$

This assumes temperature independence of transport characteristics and a small temperature gradient. Here, the first product is essentially the Carnot cycle efficiency. Thus, maximizing efficiency relies on the temperature gradient and the ZT value, establishing Carnot efficiency as the upper limit. It is clear from the eqn. 1.6 that the higher the ZT value, the better the efficiency. The numerator in the ZT in eqn. 1.5 is called the *Power Factor*.

It is evident from eqn. 1.5 that materials with high thermoelectric efficiency (ZT) need to be good at conducting electricity (high σ) but bad at conducting heat (low κ) which seems counter-intuitive because at any temperature T , the electrical conductivity and the electronic thermal conductivity (κ_e) are directly correlated according to the Wiedemann-Franz law: ($\kappa_e \propto T\sigma$) (Wiedemann and Franz, 1853). Likewise, high electrical conductivity (σ) hinders a high Seebeck value (S); as the Seebeck effect generates a voltage gradient, high electrical conductivity tends to nullify it according to Mott formula (Mott and Jones, 1958). Thus making it more challenging to acquire a high ZT . From figure 1.5c, it is clear that the optimum carrier concentration for maximizing the power factor in TE materials falls within the intermediate range of 10^{19} to 10^{20} cm^{-3} .

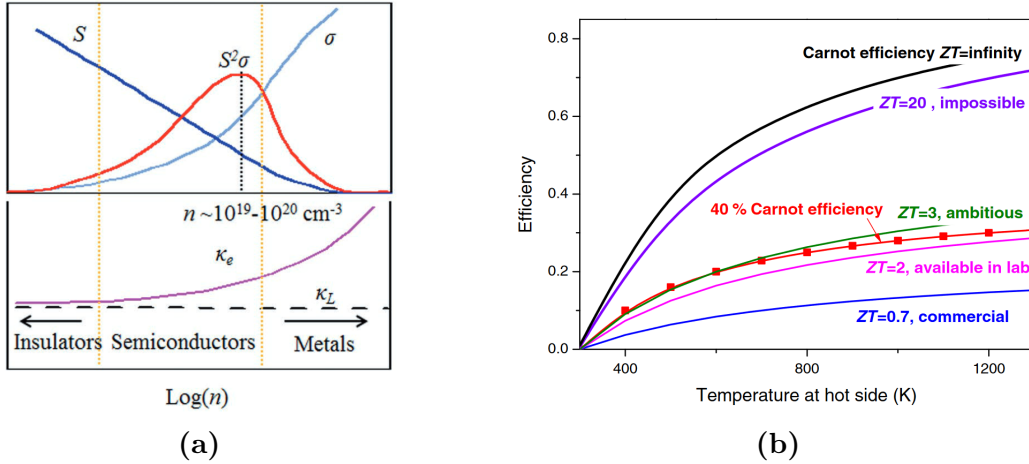


Figure 1.4: (a) Plot showing the relationship between TE transport variables (S , σ , κ_e , κ_L) and power factor ($S^2\sigma$) with carrier concentration. (Yang et al., 2017) (b) Plot displays the energy conversion efficiency for different figures of merit, keeping one side at a constant temperature of 300K. (Han et al., 2014).

As illustrated in Figure 1.5a, current commercially available thermoelectric materials typically have ZT values below 1, resulting in an average conversion efficiency of around 5%. To compete with traditional power generators, which can achieve up to 40% of Carnot's

efficiency, there's a need to enhance ZT (Chen et al., 2012). This can be achieved by either maximizing the power factor or minimizing thermal conductivity.

1.4 Strategies to optimize thermoelectric performance

To optimize TE materials for practical applications and enhance the figure of merit (ZT), addressing the trade-off between electrical and thermal conductivity is crucial. Researchers employ diverse strategies to manipulate the transport properties, aiming to boost ZT . This section explores these key strategies.

1.4.1 Electrical Transport Properties

Electrical Conductivity

The ability of a material to conduct electric current is measured by its electrical conductivity (σ). It can be expressed as: ($\sigma = ne\mu$) where n and μ are the carrier concentration and mobility, respectively. For a given value of μ , As shown in figure 1.5c, for a given carrier mobility, insulators (negligible n) show very low σ , metals at the other extent with maximum σ value, and semiconductors fall somewhere in between. Their conductivity can vary depending on the number of charge carriers, ranging from close to insulators (intrinsic) to approaching metals (highly doped) (Chen et al., 2020).

To achieve higher σ , polycrystalline TE materials are preferred over single-crystalline ones. The latter tend to exhibit higher thermal conductivity and high σ , making them less desirable for TE applications. It can be further increased by doping and creating coherent grain boundaries to increase n and μ respectively (Kim et al., 2015).

Seebeck Coefficient

The Seebeck Coefficient, also referred as thermopower, quantifies the ability of a thermoelectric (TE) material to generate an electromotive force (EMF) or voltage when exposed to

a temperature gradient. Since the efficiency is dependent on the square of this coefficient, this value is crucial in determining the efficiency of TE materials.

The Seebeck coefficient is related to the electrical conductivity (σ) and thermal conductivity (κ) of material through the Mott formula (Mott and Jones, 1958), which can be simplified by substituting σ as:

$$S = \frac{\pi^2 k_B^2 T}{3} \left(\frac{1}{n} \frac{dn(E)}{dE} + \frac{1}{\mu} \frac{d\mu(E)}{dE} \right)_{E=E_F} \quad (1.7)$$

Here, $n(E) = N(E)f(E)$ represents the carrier density at energy level E , where $f(E)$, $\mu(E)$, and e denote the Fermi-Dirac function, mobility, and carrier charge, respectively. From eqn. 1.7, it is predicted that thermopower can be improved by increasing $\frac{dn}{dE}$ (resonant states) or $\frac{d\mu}{dE}$ (carrier filtering). Using Single Parabolic Band (SPB) approximation, S can be written as:

$$S(T, n) = \frac{4\pi^2 k_B^2}{e\hbar^2} m_{dos}^* T \left(\frac{4\pi^{2/3}}{3n} \right) \quad (1.8)$$

where m_{dos}^* is the DOS effective mass. Since $S \propto m_{dos}^* n^{-2/3}$, higher m_{dos}^* and lower carrier concentration improve thermopower. (Kim et al., 2017).

Strategies to improve S include:

- **Changing carrier concentration:** Lowering n up to an optimal value without affecting S and σ by controlled chemical doping or defect manipulation can improve S as shown in figure 1.5c (Shi et al., 2020).
- **Resonant impurity states:** Introducing resonant impurity states near the Fermi level (E_F) of the host material can create a significant shift in DOS within a narrow energy range. This large change in DOS improves S , as mentioned before (Heremans et al., 2008).
- **Degenerate conducting bands:** From eqn. 1.8, it is clear that m_{dos}^* positively affects Seebeck value, but m_{dos}^* depends directly on N_v , degenerate conducting bands (Yu et al., 2019). Band degeneracy occurs when many bands have equivalent energies within a few $k_B T$, resulting from orbital or valley degeneracy. For example, Bi_2Te_3 has N_v larger than 1 but less than 6.

- **Energy filtering effect:** In TE materials, energy barriers are implemented using nanoparticles or boundary interfaces incorporated in the host matrix. Lower energy carriers are filtered out, and higher energy carriers preferentially travel across these interfaces and contribute to the Seebeck coefficient (Faleev and Léonard, 2008). Since S is understood as the entropy transfer per unit charge, the increase in the average kinetic energy of electrons due to energy filtering enhances the Seebeck coefficient.

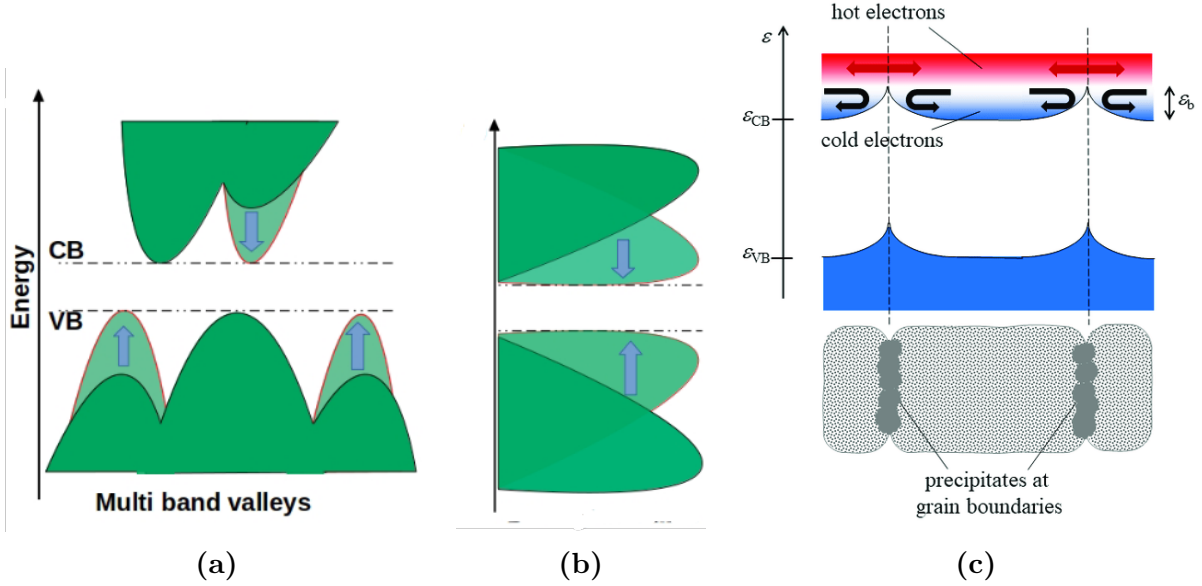


Figure 1.5: Effect of Band Engineering on Power Factor. (a) Electronic band structure demonstrating multiple carrier pockets near the Fermi level. (b) Density of states (DOS) exhibiting an increase in density near the Fermi level, characterized by a rapid slope. Adapted from Pei et al. (2012). (c) Energy filtering effects showcasing selective transport of charge carriers based on their energy levels. Adapted from Narducci et al. (2022).

1.4.2 Thermal Transport Properties

In solids, the main heat carriers include phonons, electrons, and photons, although photonic conduction typically falls outside the operational temperature range of TE devices. In a single-carrier system, thermal conductivity (κ) comprises of carrier thermal conductivity (κ_e) and lattice thermal conductivity (κ_L) (Cahill et al., 1992).

In most semiconductors, κ_L dominates significantly over κ_e . To minimize κ , we have to focus on reducing κ_L independently. Analogous to carrier transport in lattice, heat-carrying

phonons are considered as the thermal transport carriers via lattice vibration from high to low temperatures. κ_L is reduced by dampening phonon transport via phonon scattering. Phonon scattering can be achieved through mass-difference phonon scattering (Ioffe et al., 1959) and through particle inclusions, grain boundaries, and phonon-resonant scattering (Rowe, 1974), (Nolas et al., 1996). This can be attained through nanostructure engineering, which involves creating low-dimensional nanomaterials or bulk materials with nanocomposites which can significantly improve thermoelectric figures of merit (ZT) by reducing material dimensions (Chen et al., 2012).

1.4.3 Low-dimensional TE nanomaterials

Low-dimensional TE materials are a synergistic approach for achieving a higher figure of merit, ZT . It was theoretically predicted and by Hicks and Dresselhaus in the 1990s that nanoscale materials showed significant changes in TE transport properties simultaneously as they decoupled these properties, which were interrelated in the bulk, thus offering opportunities for tuning and enhancing thermoelectric performance. These were later experimentally verified by various researchers (Hicks et al., 1996), (Koga et al., 2000). Dimensional reductions produce quantum confinements and enhance DOS near Fermi level, resulting in high thermopower, as discussed in previous sections.

The combined effects of size effects and quantum confinement significantly reduce the lattice thermal conductivity (κ_L) without sacrificing electrical conductivity. Additionally, this approach can incorporate energy filtering effects (Ravich et al., 1971) and carrier pocket engineering (Koga et al., 2000), which further optimizes the material for TE applications. In this thesis, we also studied the thermoelectric properties of a few layers of Bi_2S_3 .

1.5 Bi_2S_3 as Thermoelectric Candidate

Bismuth sulfide (Bi_2S_3) has emerged as a promising thermoelectric material, gaining attention for its unique properties and potential as a non-tellurium alternative in thermoelectric applications. In comparison to industry-leading thermoelectric materials like Bi_2Te_3 , Bi_2S_3 presents several advantages, including environmental friendliness, a abundant and non-toxic

composition, and potential for enhanced thermoelectric performance (Ge et al., 2017).

Bi_2S_3 , an anisotropic orthorhombic layered system, with a direct bandgap (E_g) of about 1.3 -1.8 eV which is can tuned with varying thickness. The crystal structure (figure 1.6) exhibits anisotropic features characteristic of van-der Waals (vdW) chains where these are covalently bonded atoms in one atomic plane, with weak vdW bonds outside the plane. It shows excellent TE properties like low thermal conductivity and effective mass. But it couldn't be exploited much because of its low electrical conductivity due to its low intrinsic carrier concentration (Messalea et al., 2020).

To overcome this, we adopted the strategy of nanostructuring the bulk, specifically using 2D thin films. The decrease in thermal conductivity with reduced thickness, attributed to surface phonon scattering, is complemented by an increase in electrical conductivity, potentially influenced by alterations in the band structure due to its lamellar structure like graphene (Lee et al., 2016). Due to the weak inter-layer interaction, it allows for the synthesis of Bi_2S_3 thin films through top-down approaches such as exfoliation which we have followed as our synthesis.

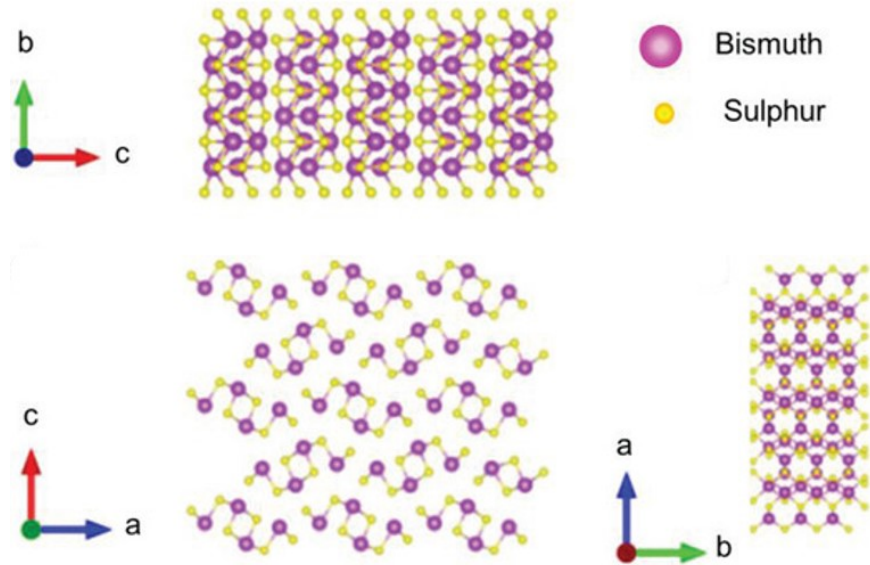


Figure 1.6: Geometrical Structure of Bi_2S_3 : Ball-and-stick model illustrating the crystal structure of Bi_2S_3 from different axes. Purple and yellow balls represent bismuth and sulfur atoms, respectively. (Messalea et al., 2020)

1.6 Scope and limitation of this Thesis

This thesis places a central emphasis on an extensive examination of the Seebeck coefficient property within Bi_2S_3 thin films. The rationale for this research is based on the existing groundwork in thermoelectric exploration, particularly in bulk Bi_2S_3 , which has extensively covered properties such as electrical conductivity, thermal conductivity, and the Seebeck coefficient. However, the nanoscale thermoelectric properties of Bi_2S_3 thin films have remained relatively underexplored (Liufu et al., 2007), (Ji et al., 2023), (Mulla et al., 2023).

It's essential to clarify that our focus is exclusively on the Seebeck coefficient, and we are not examining all thermoelectric transport properties in this thesis. Consequently, we acknowledge that predicting the figure of merit for the thin film material is beyond the scope of our current investigation.

One limitation is the utilization of an indirect method for measuring the temperature difference. Our methodology involves resistive measurements calibrated using contact pad temperature coefficient of resistance (TCR) literature values. While this approach allows for the assessment of the Seebeck coefficient, it introduces potential sources of uncertainty and assumes the accuracy of TCR values from the literature.

Chapter 2

Experimental Methods

The experimental methods employed in this thesis fall into three categories: i) Thin film synthesis, ii) Device fabrication, iii) Characterization techniques, and iv) Transport properties measurement methods.

Within the scope of my thesis, which concentrates on evaluating the Seebeck coefficient in Bi_2S_3 thin films using a custom lab-built setup, it is essential to detail the synthesis methods and device fabrication techniques utilized in my research. Additionally, it sheds light on the methodologies employed for structural characterization. Finally, the chapter outlines the experimental procedures applied in my DUT for thermoelectric characterization.

In this thesis, we have worked on two different types of devices,

- Microscale: Spray-coated Bi_2S_3 device
- Nanoscale: Mechanical exfoliated Bi_2S_3 film

The fabrication techniques of both types of devices are discussed below.

2.1 Sample Synthesis

The preparation of the sample is divided into two distinct methodologies, each tailored to specific scales: the microscale film preparation involves utilizing the spray pyrolysis technique, which will allow us to tune the film thickness through process parameters, while the nanoscale film extraction is achieved through micromechanical exfoliation. For achieving atomic-thin layers, the mechanical exfoliation method is particularly effective (Novoselov et al., 2004). This technique is notable for producing lamellar-structured materials like Bi_2S_3 with just one or a few layers of atoms (Messalea et al., 2020).

2.1.1 Spray Pyrolysis

The spray pyrolysis technique is highly utilized in thin film deposition and material science. This method is a flexible and effective way to create thin films, providing precise control over their composition and thickness. It also requires moderate operating temperatures (between 100 and 500°C) and doesn't require high-quality targets, substrates, or vacuum conditions.

During the spray deposition process, a precursor solution is atomized and propelled onto the substrate by a neutral gas, typically nitrogen. Chemical reactions ensue among the constituents within the fine droplets, leading to the deposition of the desired compound onto the substrate surface. The careful selection of reactants is crucial to ensure that any undesired by-products have sufficient volatility at the deposition temperature to be effectively removed. Additionally, the uniformity of the deposition process is facilitated by employing various arrangements, such as moving nozzles or substrates, to ensure consistent coating across the substrate surface.

Film characteristics depend on factors like spray speed, substrate temperature, droplet dimensions, ambient conditions, carrier gas, and post-deposition cooling rate. Spray nozzle-to-substrate distance, substrate temperature, precursor solution concentration, and sprayed volume actively influence the thickness (Patil, 1999).

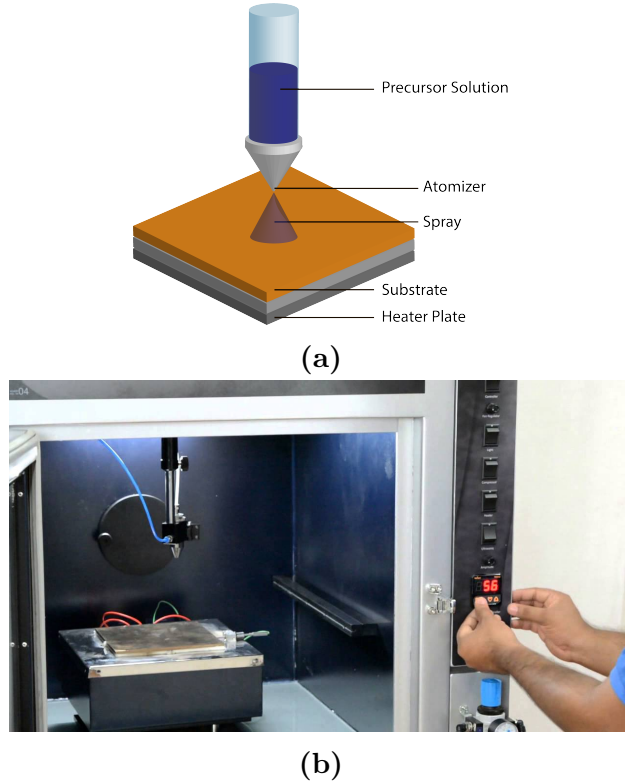


Figure 2.1: (a) Schematic of the spray deposition process. (b) Image of the *Holmarc* Spray Pyrolysis Equipment obtained from the Holmarc website.

Procedure:

To fabricate Bi_2S_3 thin films via spray pyrolysis, 1g of Bi_2S_3 crystals (sourced from Sigma Aldrich) is ultrasonicated in 100 ml of DMF to prepare the precursor solution. This solution is then spray-coated onto a cleaned copper foil at 426 K, utilizing nitrogen as the carrier gas to ensure uniform deposition. Each layer is coated at a rate of $200 \mu\text{l}/\text{min}$ to precisely control the film thickness. Following coating, the Cu foils are immersed in a PC solution to protect the film from both sides. The bottom PC layer is selectively removed to expose the copper foil. Subsequently, the substrates are immersed in a freshly prepared ferric chloride etchant solution for 3-4 hours, facilitating controlled Cu foil etching and the formation of freestanding Bi_2S_3 films. Washing with chloroform removes the top PC layer, yielding the desired thin film structure (Nandi and Misra, 2019). The steps are illustrated in figure 2.2

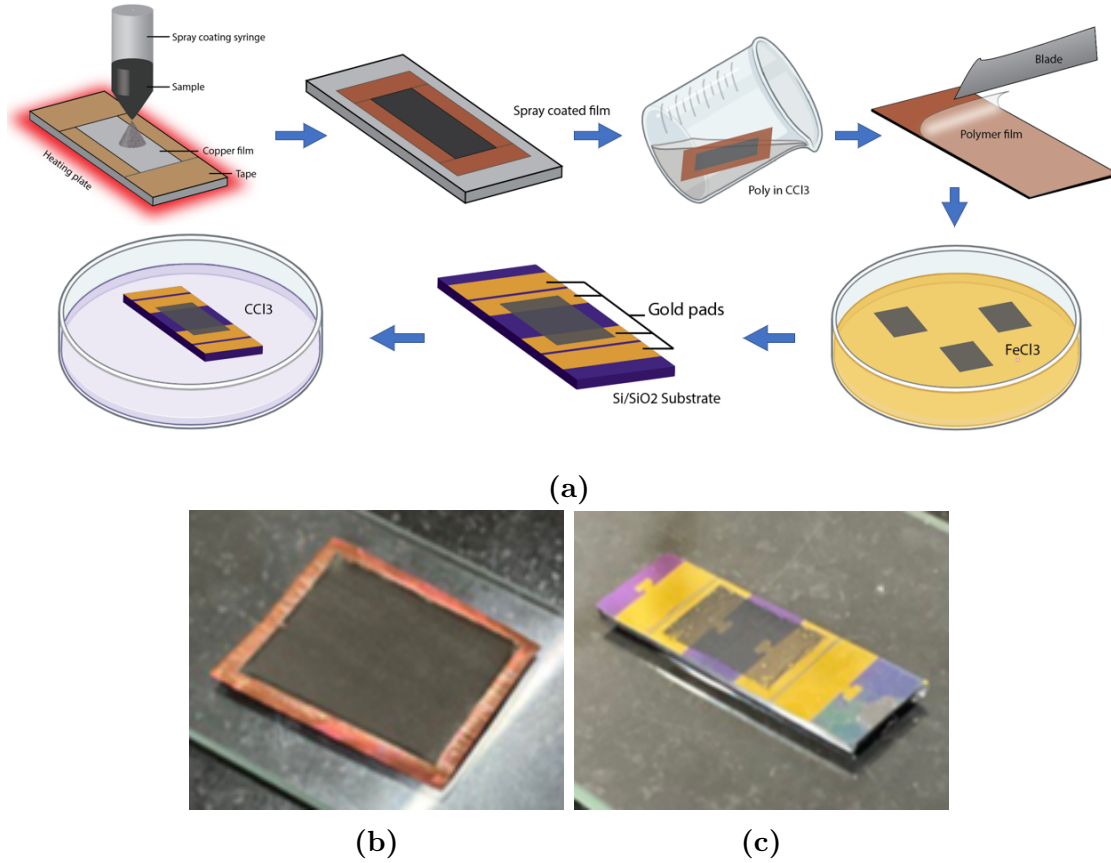


Figure 2.2: (a) Illustration depicting the steps involved in fabricating thin films using the spray pyrolysis technique and post-processing to produce thin films. Illustrated using Adobe Illustrator. (b) Spray-coated copper film. (c) Transferred spray-coated device onto the Si/SiO_2 substrate

2.1.2 Micromechanical Exfoliation

The mechanical exfoliation method, often referred to as the "Scotch tape method" or adhesive tape exfoliation, is a robust technique for obtaining layered 2d structures from bulk graphite or analogous layered structures, for which Novoselov and Geim were recognized with the Nobel Prize in Physics in 2010.

Bi_2S_3 crystals, like graphite, have a lamellar structure with layers of bismuth and sulphur held together by van der Waals interactions (as shown in). These layers can be viewed as two-dimensional (2D) materials similar to graphene. The Bi_2S_3 crystal's van der Waals (vdW) interactions are weak compared to the adhesive forces between scotch tape and sample planes.

External mechanical force can cause the Bi_2S_3 crystal to cleave along out-of-plane layers of bismuth and sulphur atoms. Atomically layered materials have strong in-plane bonding, resulting in high-quality and continuous exfoliated 2D crystal films (Novoselov et al., 2005).

Procedure:

Instead of conventional exfoliation directly onto the substrate, a method involving soft exfoliation and transfer was employed. This process utilized a polydimethylsiloxane (PDMS) stamp (Gel-Film[®] WF supplied by Gel-Pak) instead of a hard substrate. Initially, the parent Bi_2S_3 flake, obtained from the bulk n-type crystal sourced from 2D Semiconductors Corporation, was repeatedly peeled using blue Nitto tape (Nitto Denko Co., SPV 224P). This approach aimed to address challenges related to tearing kinetics and other mechanical and geometrical properties of the materials. Subsequently, a suitable flake was selected using an optical microscope for dry transfer onto the device with appropriate magnification. Upon bringing the PDMS stamps with Bi_2S_3 into contact with the Si/ SiO_2 substrate, the Bi_2S_3 flakes dissociated from the surface of PDMS and were released onto the substrate (Ceballos et al., 2014), (Tripathi and Misra, 2021).

2.2 Device Fabrication

The fabrication of the spray-coated thin film device are detailed in the Appendix.

For the nanoscale device, the focus shifts to the fabrication and characterization of devices utilizing exfoliated flakes. The identification of atomically thin 2D flakes was facilitated by employing an optical microscope (NIKON Eclipse NE 100 microscope), where the number of layers was estimated approximately by evaluating their opacity and contrast. Following this, a suitable thin flake was selected for the dry transfer onto the pre-deposited microelectrodes on Si/ SiO_2 using electron beam (e-beam) lithography, a topic discussed in the subsequent section.

2.2.1 Electron beam lithography

Electron Beam Lithography (EBL) is an advanced nanofabrication technique that uses a focused beam of electrons to precisely pattern substrates at the nanoscale. It is used here to fabricate the device's electrical structure, involving metal electrodes, heater lines, and connection pads for electrical measurements.

Initially, a resist-coated substrate was prepared utilizing a bilayer-positive resist which acts as the canvas for the nanoscale design. The electron beam is precisely controlled to expose specific regions of the resist, causing a transformation in their chemical or physical properties. The lithography process was conducted using the Raith e-line system in *National Nanofabrication Centre* (NNFC) (Figure 2.3a). We utilize two positive e-beam resists by 'Micro Chem Corporation,' PMMA 495 K A4 as the bottom layer and PMMA 950 K A4 as the top layer. The higher molecular weight of PMMA 950 K results in a slower development rate compared to PMMA 495 K. This difference is exploited to achieve improved lift-off after metal deposition. Both e-beam resists were spin-coated and cured to form a uniform hard resist layer. The contact pattern and pads were designed using Clewin 5.1 and Raith eLiNE software. The pattern was selected by exposing design areas to an e-beam dose of $250\text{--}300\text{ }\mu\text{C}/\text{cm}^2$. Then, the wafers undergo immersion in a developer solution (1:3 volume of MIBK: IPA) for a developing time of 40 seconds. This step selectively dissolved the PMMA in the regions exposed to the electron beam. To create contacts on the developed samples, the developed samples are metalized using an e-beam evaporator (Techport system) (Figure 2.3c). A chromium ash deposition is performed to eliminate oxidation from the chromium pallets, enhancing the vacuum while covering the sample with the shutter. Subsequently, a 5 nm layer of chromium is deposited on the electrodes. On top of this 5 nm seed layer of chromium, 50 nm of gold is deposited. The final step involved a lift-off process by immersing in acetone to selectively dissolve the metal film except for the areas patterned by the developed PMMA. This process resulted in Cr/Au microelectrodes with a thickness of $5/50\text{ nm}$.

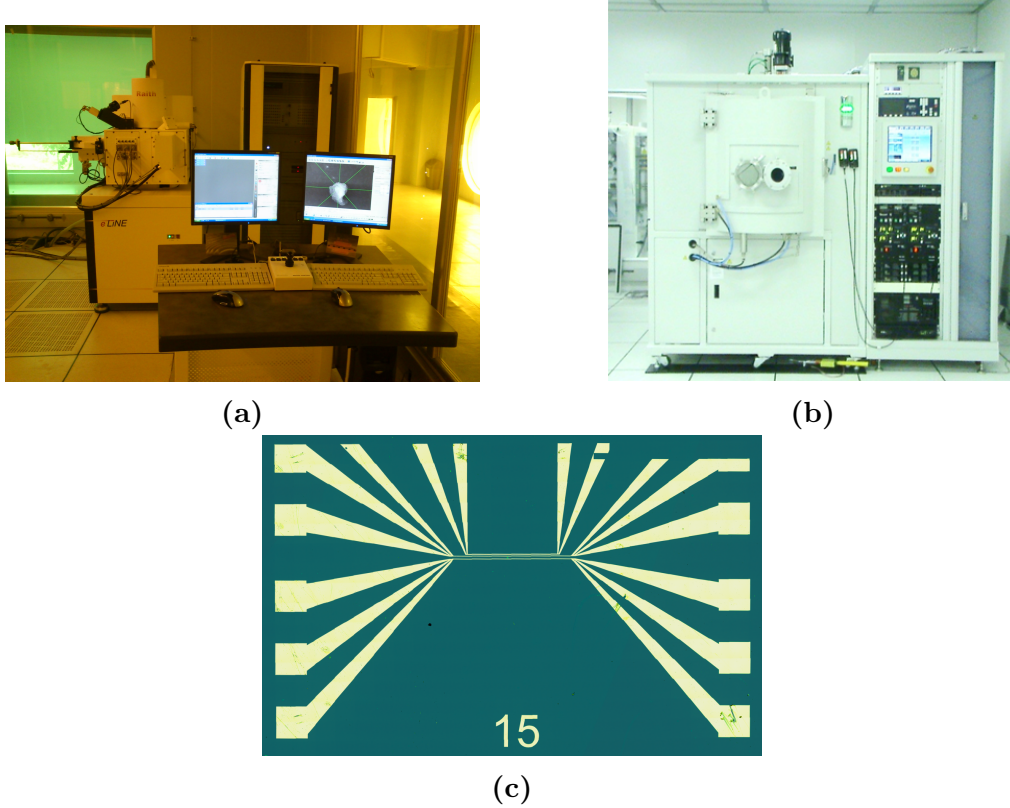


Figure 2.3: (a) *Raith eLINE* Lithography system, (b) *Techport* Ebeam Evaporator, housed in CeNSE, National Nanofabrication Centre (Source: CeNSE website). (c) 50x stitched image of deposited microelectrodes with 15 μm spacing between the source and drain line.

2.2.2 Dry-transfer Process

Upon identification of a thin flake, the subsequent step involves the dry transfer of the flake developed by Castellanos-Gómez et al., (2014) onto the microelectrodes markers using the *SUSS MicroTec* MJB4 Mask aligner system, as illustrated in figure 2.4a. The acceptor substrate with the microelectrodes is positioned at the center of the lower substrate stage and fixed using double-sided tape. The glass slide containing the PDMS stamp is attached to the mask aligner glass plate and vacuum-pressed onto the mask holder with the flakes facing the acceptor substrate. The micromanipulator has two three-axis motion frames for controlling the position and focal plane of the microscope components on the upper frame and for controlling the position and vertical movement of the acceptor substrate on the bottom stage. Notably, the mask holder remains stationary and is secured between the two

microscope frames. A central opening in the upper stage allows access to the lower stage.

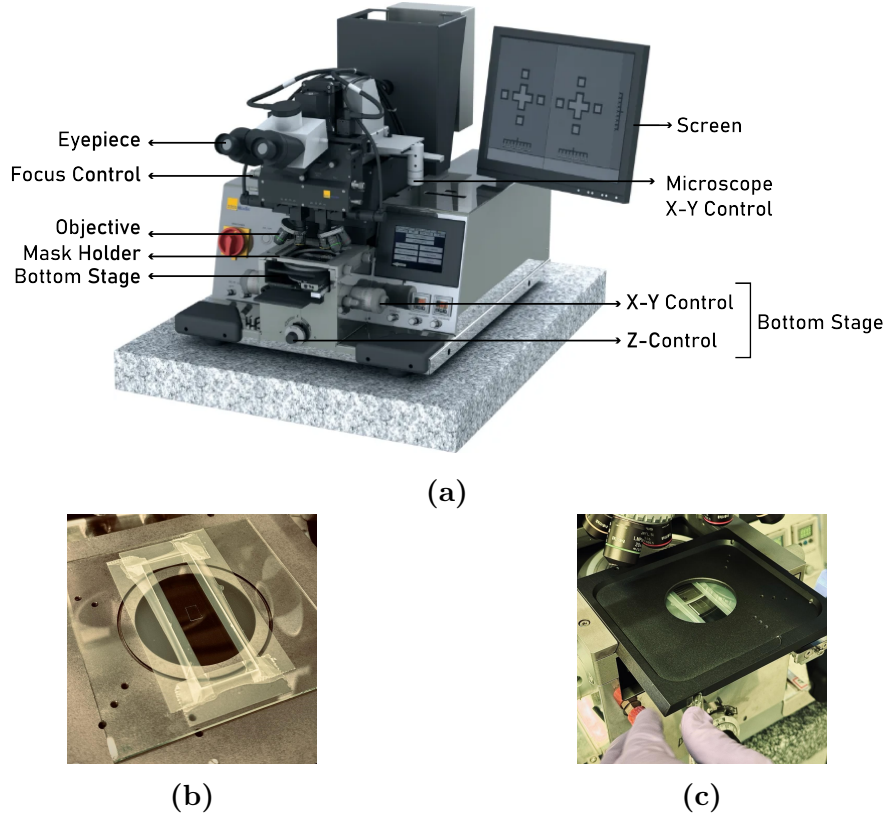


Figure 2.4: **a)** Image of SUSS MicroTec MJB4 Mask aligner system (source: SUSS MicroTec website). **b)** Glass slide with PDMS attached to the mask aligner glass plate. **c)** Upper stage with PDMS aligned at the center cut-out.

The transfer process is set up by keeping the mask holder with the PDMS facing the target substrate placed at the bottom stage through the central cutout of the mask holder. The flake on the PDMS can be coarsely aligned by monitoring the microscope using the three-axis micrometer motion of the upper frame. Similarly, using the lateral freedom of the bottom stage, the target markers are aligned with the flake. By keeping the focus on the focal plane of the flake, the bottom stage is brought closer using the z-axis control, so the marker electrodes are brought closer to the focused plane. Now, since both flake markers are visible, fine position adjustments are done. When the PDMS comes into contact with the flake, a film lamination is gently formed through the flake. Gentle pressure is applied to the substrate surface to ensure flatness and minimize air bubble formation during transfer. The transfer mechanism relies on the viscoelastic properties (Meitl et al., 2006), where flakes

adhere to the stamp surface due to the adhesion of the viscoelastic material. By gently moving down the bottom stage, the viscoelastic stamp gradually peels off from the target substrate, releasing the flake from the stamp and dropping it on the target substrate at the marker location. Once the substrate is moved down the stage, we will not observe the flake on the stamp plane if it has been transferred successfully, and it can be checked at the substrate plane for a successful flake transfer. The step-by-step process is schematically illustrated in figure 2.5. Some of the successful flake-transferred devices are shown in figure 2.6

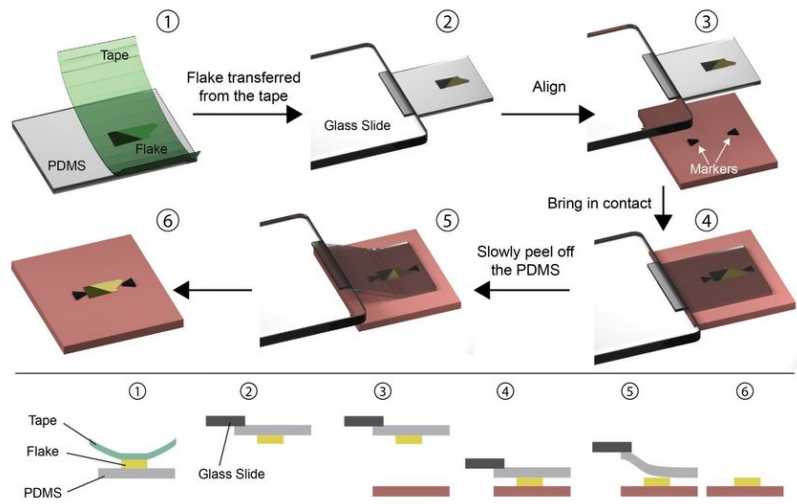


Figure 2.5: PDMS-based deterministic transfer method: Steps involved (1-6) in the soft-mechanical exfoliation process of 2D flakes using a viscoelastic material (PDMS) and dry transferring onto pre-deposited electrodes using a micromanipulator.

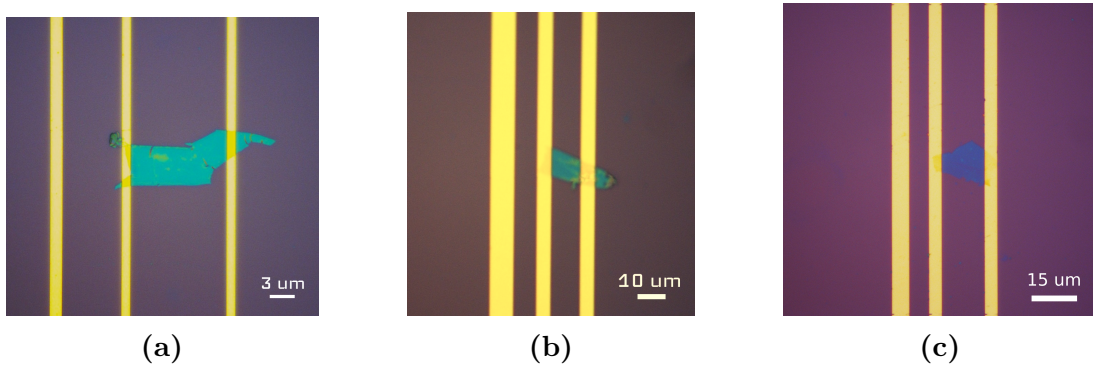


Figure 2.6: Flake-transferred Devices: Optical images of three flakes transferred between the gold contact lines separated by a) $12\ \mu\text{m}$, b) $10\ \mu\text{m}$, and c) $15\ \mu\text{m}$.

2.2.3 Packaging and Wire bonding

The packaging process involves placing devices inside a leadless ceramic chip carrier (LLC) with 44 I/O ports. The wafer is diced to fit into the chip carrier's cavity and bonded with silver epoxy at the base. Using the wedge bonding method with a West-Bond Luxuray II manual wire-bonder (Fig. 2.7a), device contact pads are connected to I/O pads with 25-30 μm wire. Thermal energy from a heater plate aids bonding, with ultrasonic power adjusted for each bond. The wedge presses the wire against the IC bond pad, creating ultrasonic bonds. Forward bonding prevents edge shorts. Finally, the wire-bonded chip is housed in a PLCC socket and soldered with external leads onto a breadboard for electrical testing.

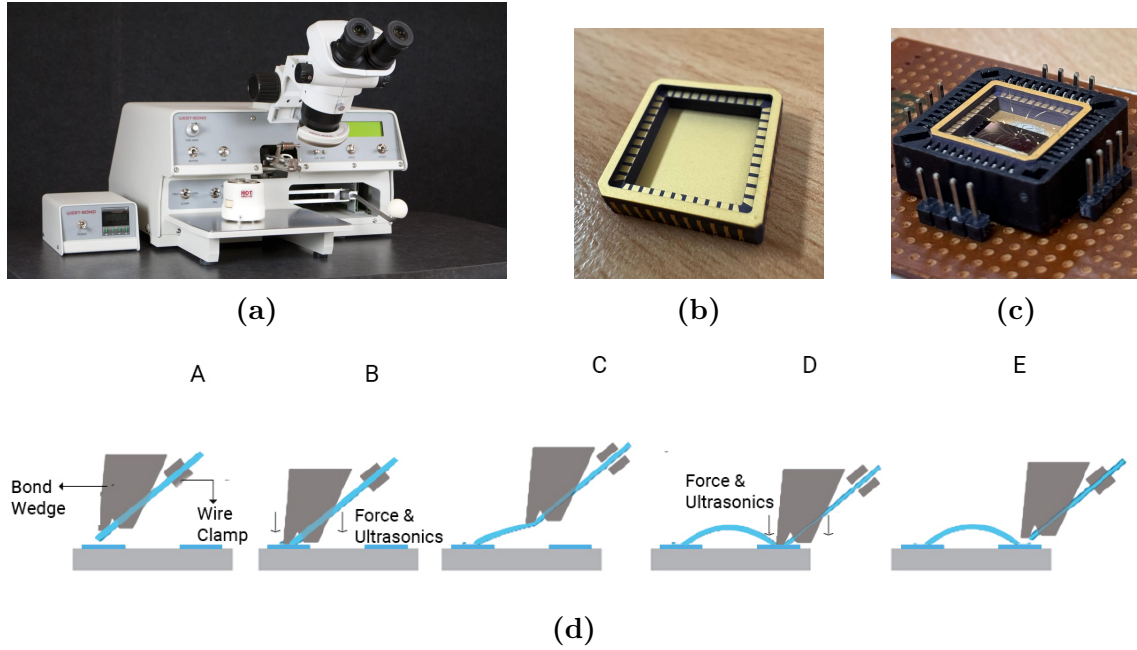


Figure 2.7: a) West-Bond Luxuray II manual wire-bonder (Source: WEST-BOND website), b) Leadless ceramic chip carrier with 44 I/O ports, c) Fully assembled device for electrical measurement and d) Schematic outlining the wire bonding steps (A-E) for connecting two contact pads (Team, 2023).

2.3 Characterisation Techniques

Following exfoliation onto the PDMS stamp, the thickness of the flakes can be initially estimated using the contrasting optical response observed in microscopic images. This approach allows for the targeted transfer of the flake onto the pre-prepared Si/SiO₂ substrate containing the microelectrodes. For a comprehensive characterization, the fully fabricated device are characterized using Raman spectroscopy and Atomic Force Microscopy (AFM).

2.3.1 Optical Microscopy

Optical contrast assessment provides a rapid and efficient method for approximating the number of layers within Bi₂S₃ flakes. Atomically thin flakes display noticeable contrast against the substrate, allowing their observation using the *NIKON Eclipse NE 100* optical microscope. The NIS-Elements Imaging software facilitates real-time image capture and dimensional analysis, aiding in the precise selection of flakes with desired dimensions for subsequent transfer between pre-fabricated electrodes. This approach serves as a preliminary screening technique, allowing for the efficient identification of flakes with the appropriate number of layers from a pool of cleaved flakes, ultimately facilitating their selection for dry transfer processes. However, optical contrast techniques have limits, especially for extremely few layers, and may lead to false thickness estimations due to interference (Ni et al., 2007).

2.3.2 Atomic Force Microscopy

Atomic force microscopy (AFM) is used to characterize thickness and surface profile. Measurements are conducted using *Park NX20 AFM* at CeNSE, Micro-Nano Characterization Facility (MNCF). This technique uses the non-contact mode with a *Tespa V2* probing tip. In this mode, the tip oscillates near the sample surface, detecting the electromagnetic force and associated phase shift as it scans the area while minimizing physical contact. This information can be used to reconstruct the sample's topography and determine its height, allowing for the precise measurement of flake thickness.

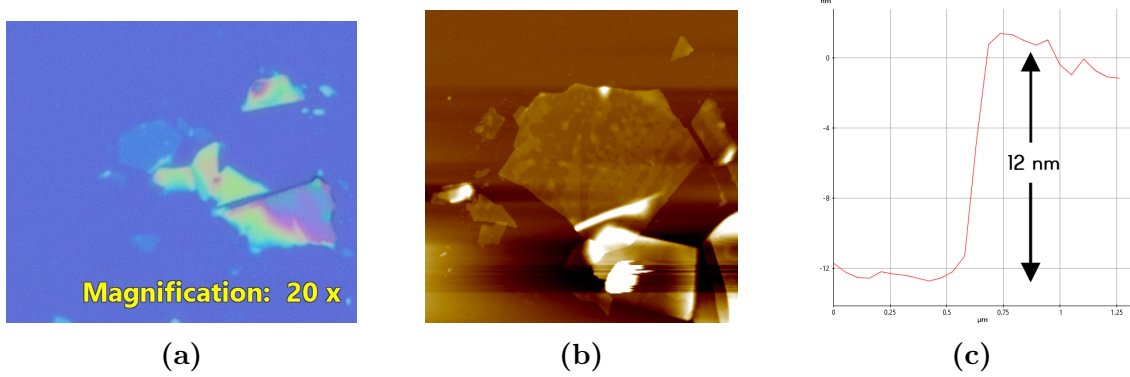


Figure 2.8: a) Optical image of a thin Bi₂S₃ flake at $20X$ magnification. b) AFM image of the same flake. c) Thickness profile of the flake, indicating a thickness of 12 nm.

2.3.3 Raman Spectroscopy

Raman spectroscopy offers a rapid, non-invasive, and non-destructive method for analyzing the structural, compositional, and electronic properties of 2D flakes. This technique relies on the inelastic scattering of photons, generating a unique "fingerprint" of vibrational modes within the material (Smith, 2019). Therefore, this technique finds extensive applications in material identification (Kudelski, 2008), probing structural and crystalline (Malard et al., 2009), non-contact temperature measurement (Yue and Wang, 2012), and examining phenomena related to thermal energy transport in research (Yuan et al., 2017). Although each Raman-active material exhibits a unique spectral signature, the signal strength isn't solely determined by the material itself. Two key factors play a role: the sampling volume, which refers to the portion of the material interacting with the laser light, and instrumental parameters like the frequency and intensity of the excitation laser, the efficiency and sensitivity of the detector, and the measurement time. Research has demonstrated that by carefully altering these variables, one may determine the relative thicknesses of the films by studying changes in Raman signal intensity across numerous thin-film samples (Koh et al., 2010), (Li et al., 2012), (Li et al., 2015). Various research groups, (Huang et al., 2018), (Trentelman, 2009), and (Zumeta-Dubé et al., 2014), have extensively explored the Raman spectra of both bulk and nanosheet Bi₂S₃ and consistently identify characteristic peaks corresponding to the transverse A_g vibration modes at 100 cm^{-1} and 237 cm^{-1} , and the longitudinal B_{1g} vibration modes at 187 cm^{-1} and 264 cm^{-1} as shown in figure 2.9b. The Raman spectroscopy employed in our studies utilized the *WITec alpha 300* (figure 2.9a) system at room temperature, uti-

lizing a laser source of 532 nm.

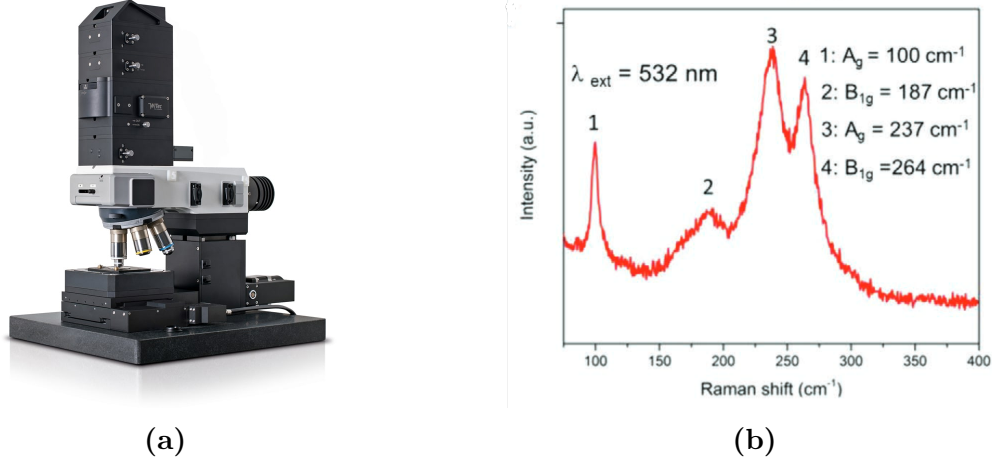


Figure 2.9: a) Image of the WITec alpha300-R Raman Spectroscopy Instrument. (Source: WITec Website) b) Plot showing the characteristic Raman peaks for Bi_2S_3 at 100 cm^{-1} , 187 cm^{-1} , 237 cm^{-1} , and 264 cm^{-1} . (Source: (Zumeta-Dubé et al., 2014))

2.4 Transport Property Measurement Techniques

In this section, we look at the experimental methods used to evaluate the in-plane thermal and electrical transport properties of our fabricated and packaged Bi_2S_3 thin film devices to comprehend their thermoelectric characteristics.

Our focus is on determining the Seebeck coefficient of the sample. Initially, we used a microscale device with a Peltier module for controlled heating and established a temperature gradient across the thin film. Non-contact temperature measurement was achieved with a laser thermocouple, and the open-source voltage across the thin film was measured using a Keithley 2450 SourceMeter Unit. Transitioning to the nanoscale, we explored the thermal and electrical transport properties of exfoliated Bi_2S_3 flakes. Following Chen et al.'s 2023 methodology, we employed four-probe resistance measurements for determining the Seebeck coefficient. This precise measurement involved introducing a DC current-flowing heater line near one side of the flake to maintain a constant and known temperature gradient. The temperature difference across the flake was determined using the Temperature Coefficient of Resistance (TCR) for the Cr/Au gold lines. The following sections will detail the macroscopic

Peltier heating setup and the nanoscale four-probe measurement technique.

2.4.1 Microscale Peltier-heating Setup

The device fabrication and packaging have been discussed in Appendix. We employed a Peltier module (TEC1-12706) to generate a lateral temperature gradient across the Bi_2S_3 thin film. Placed perpendicular to the film, the Peltier module's heater side faces the sample as shown in figure 2.10. This configuration served as our thermoelectric heater for measurements. The Peltier module is closely aligned and joule-heated to induce a lateral temperature gradient across the thin film. Notably, the Peltier heating surface is considerably larger than the dimensions of the thin film. To ensure a unidirectional temperature gradient along its length, precautions were taken to prevent any temperature variations across its width, which could potentially interfere with measurements. A laser thermocouple was employed for precise temperature measurements, allowing us to determine the temperature difference across the thin film sample. The calibration of the Peltier module was conducted by recording temperatures at various DC input voltage settings, providing accurate control over the temperature gradient.

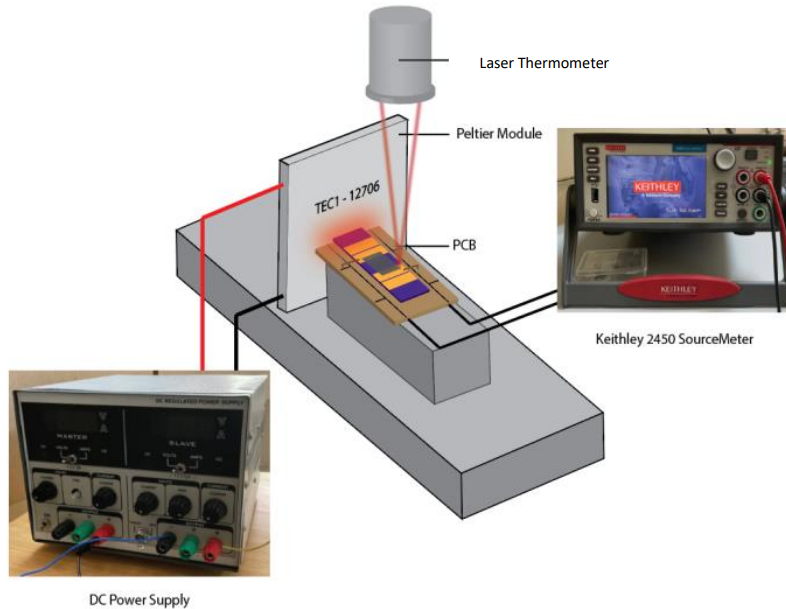


Figure 2.10: Electrical measurement setup of Microscale device: Illustration showing measurement setup for the microscale Peltier heating setup. Illustrated using Adobe Illustrator.

The electrical properties (I-V) of the sample were characterized using the Keithley 2450 SourceMeter, where small voltages were swept to evaluate the ohmic behavior. We monitored the thin film's current characteristics over time by applying a predetermined temperature gradient with the Keithley 2450 SourceMeter. This involved applying a pulsated voltage bias with a slight current limit, allowing us to observe how the film responded to temperature changes and its consequent impact on current flow. This procedure is the foundation for understanding the macroscale thermoelectric properties of the Bi_2S_3 thin film.

2.4.2 Four-probe resistance measurement technique

The DUT consists of a Bi_2S_3 flake positioned between two elongated gold (Au) lines, each approximately $500\text{ }\mu\text{m}$ long. These lines are significantly larger than the flake, ensuring a uniform lateral temperature gradient across its length. A separate, parallel Au line functions as a heater. The contact lines serve a dual purpose: electrical transport measurements (source and drain) and resistance thermometry. The four-probe technique is employed to minimize the impact of external factors like contact resistance during electrical measurements.

Two Keithley SourceMeter Units (models 2450 and 2602) were employed to simultaneously measure the four-probe resistances of the source and drain lines. This involved applying a voltage bias across the metal lines and measuring the resulting current to determine their resistance. Simultaneously, a DC heating current was supplied from a VAR Tech DC Power Supply 3005B. This setup allowed for the monitoring of resistance changes in both lines under varying DC heater voltages. To ensure the integrity of the metal lines, the resistance change under varying heater voltages was calibrated using a reference device (DUT) without the Bi_2S_3 flake. This calibration involved applying pulsed heater voltages and analyzing the incremental resistance change for each voltage step. The pulse duration was optimized based on the observed saturation time for both the rise and subsequent resistance return to its initial value at each step.

Additionally, we used the Probe Station – *SÜSS MicroTec PM5* from CeNSE, Micro-Nano Characterization Facility (MNCF), to measure the resistance of the metal lines in another DUT to eliminate the need for wire bonding and other additional connections.

From the measurements of the four-point resistances, temperature can be inferred using

the relationship between resistance and temperature, given by:

$$R = R_{initial}[1 + \alpha(T - T_{initial})], \quad (2.1)$$

where R represents the conductor resistance at temperature T , $R_{initial}$ is the initial conductor resistance at the initial temperature, and α is called the Temperature Coefficient of Resistance (TCR), defined as the resistance change per unit change in temperature or the slope of the R-T characteristics. For metals, this coefficient is positive. Therefore, from this relationship, the temperature difference can be determined. We utilized literature values to obtain the TCR of gold films of our desired thickness (Oliva and Lugo, 2016).

2.4.3 Seebeck Coefficient

Once the temperature gradient had been calibrated using the four-probe resistance measurements, we measured the open-source voltage across the metal lines. With the Bi_2S_3 flake acting as the channel between the two lines, this measurement was performed for varying heater voltages.

This step aimed to investigate the thermoelectric behavior of the Bi_2S_3 flake. As the heater voltage increases, the temperature gradient across the flake also increases. This temperature difference can induce a voltage across the flake due to the Seebeck effect, a phenomenon observed in thermoelectric materials. By recording the open-source voltage as a function of heater voltage, we can obtain a relationship between the applied temperature gradient and the generated voltage, thereby determining the Seebeck coefficient of the thin film sample.

Chapter 3

Results and Discussion

This chapter presents the observations and analyses obtained from the experiments conducted on Bi_2S_3 thin film samples. It explores the characterization results obtained at both the macro and nanoscale, providing insights into the thermoelectric properties of these films. The findings from various characterization techniques will be presented and discussed, aiming to establish a correlation between the observed micro/nanoscale behavior and the overall thermoelectric potential of Bi_2S_3 thin films.

3.1 Sample Characterisation

Our examination of the sample's characteristics primarily concentrates on the nanoscale, particularly regarding the mechanical exfoliation of thin film samples. While we opted not to extensively characterize at the microscale, our reasoning is based on the assumption that nuanced features at this level may not significantly impact the macroscale, where films are synthesized via spray pyrolysis with a controlled deposition rate.

For our nanoscale characterization, we conducted a comprehensive analysis of mechanically exfoliated flakes. Initially, we used optical imaging to identify potential flakes of interest, followed by a detailed examination of their thickness profiles using Atomic Force Microscopy (AFM) with dedicated software (*Park Systems XEI*), which allowed us to select thinner and more suitable flakes for subsequent device fabrication and transport measurements.

From the optical image of one of the mechanically exfoliated flakes, depicted in Figure 2.6c, we obtained an initial estimate of its thickness, indicating that it comprised a few layers rather than being a bulk flake. This information guided our selection process for the transfer process onto electrodes. Subsequently, we assessed the thickness and surface profile of the transferred flakes to ensure proper contact with the electrodes. The AFM images and thickness profile of one of our successful devices are illustrated in Figure 3.1.

We employed Raman spectroscopy to analyze the Raman peaks, utilizing a 532 nm laser source. The transverse A_g vibration modes were detected at 100.9 cm^{-1} and 237.6 cm^{-1} , while longitudinal B_{1g} vibration modes were observed at 187.1 cm^{-1} and 261.4 cm^{-1} , as depicted in Figure 3.2. These findings align closely with previously reported values, as discussed in Section 2.3.3.

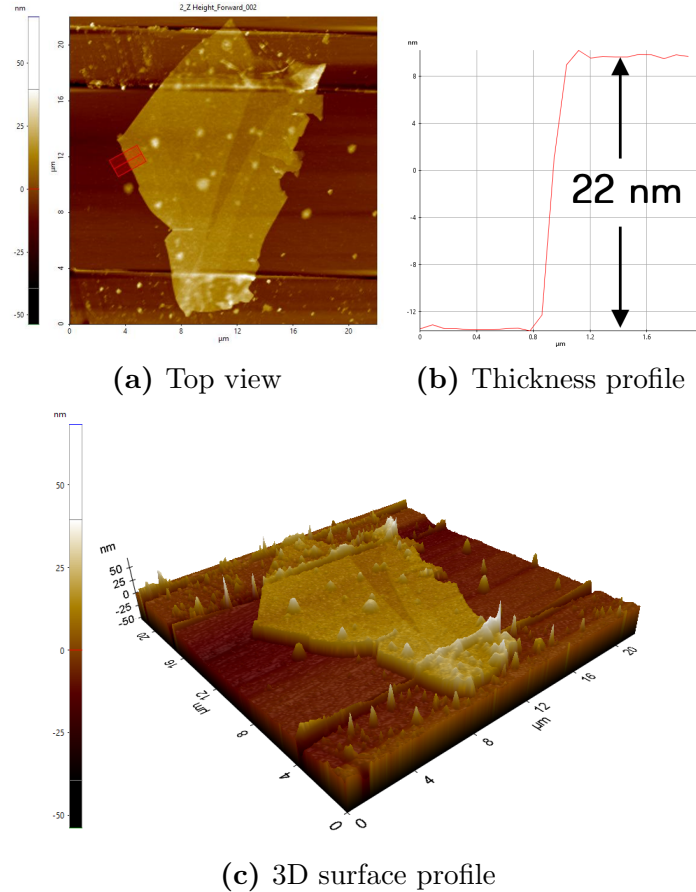


Figure 3.1: AFM Imaging: Depicts the thickness profile of a flake situated between the metal lines on the device, measuring 22 nm in thickness.

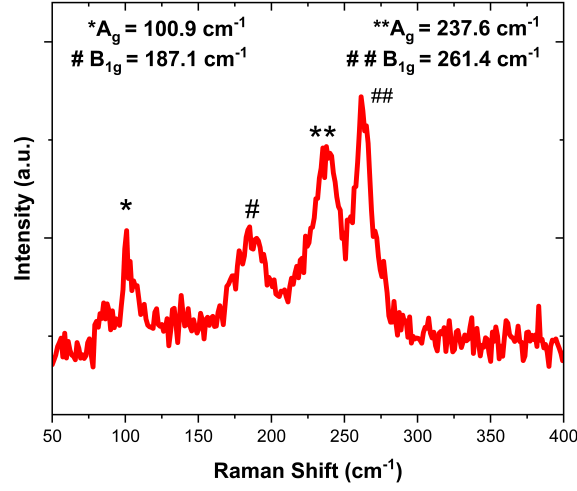


Figure 3.2: Raman Spectra : Raman Spectra of few layers of Bi₂S₃ showing transverse (A_g) and longitudinal modes (B_{1g})

3.2 Transport and Electrical Properties

3.2.1 Microscale Device

The evaluation of microscale transport properties serves as a checkpoint to understand the material's response to temperature gradients, understanding of how the thin film responds to localized temperature changes, especially in terms of its thermoelectric behavior, assessing whether the Seebeck effect is evident. Our approach involved establishing a simple yet effective setup to induce a temperature gradient across the spray-coated film as detailed in the device fabrication discussed in the previous chapter. We assumed a uniform lateral heating distribution across the film to maintain simplicity in our experiment.

We initially calibrated the Peltier module by systematically measuring temperature variations using a non-contact laser pyrometer at fixed voltage supply settings as detailed in Table 1. We also checked the IV characteristics of the film without any heating to verify the ohmic connections sweeping voltage from -0.1 to 0.1 V.

Peltier Voltage (V)	Heater Temperature ($^{\circ}\text{C}$)
0	$\sim 32^{\circ}(\text{RT})$
2	$\sim 45^{\circ}$
3	$\sim 50^{\circ}$
4	$\sim 66^{\circ}$
5	$\sim 80^{\circ}$
6	$\sim 90^{\circ}$

Table 3.1: **Peltier Module Temperature Calibration**

Since surface temperature measurements were conducted using a laser pyrometer focused on the Peltier module, it's important to note that this method is susceptible to fluctuations arising from background conditions. Therefore, the recorded temperature is an approximation rather than an exact value.

After calibration, it is kept in contact with the film substrate in order to transfer the heat. To investigate the thin film response to a temperature gradient, we monitored the I-V characteristics with and without Peltier heating (Figure 3.3).

The analysis of the I-V curve (Figure 3.3a) indicates that all connections exhibit ohmic behavior, confirming the continuity of the spray-coated film. At 0 V Peltier voltage, the I-V curve displays a slope corresponding to the resistance of the entire circuit, which encompasses the film channel. Introducing step voltages ranging from 2-6 V Peltier voltage results in varying slopes in the I-V curve for each step. Each step voltage is allowed time to achieve a steady state, reflecting the maximum current corresponding to the applied voltage. Figure 3.3b illustrates an increase in the slope of the I-V curve at positive voltage ranges, signifies a concurrent decrease in resistance, indicating the impact of heating on the transport properties of the film.

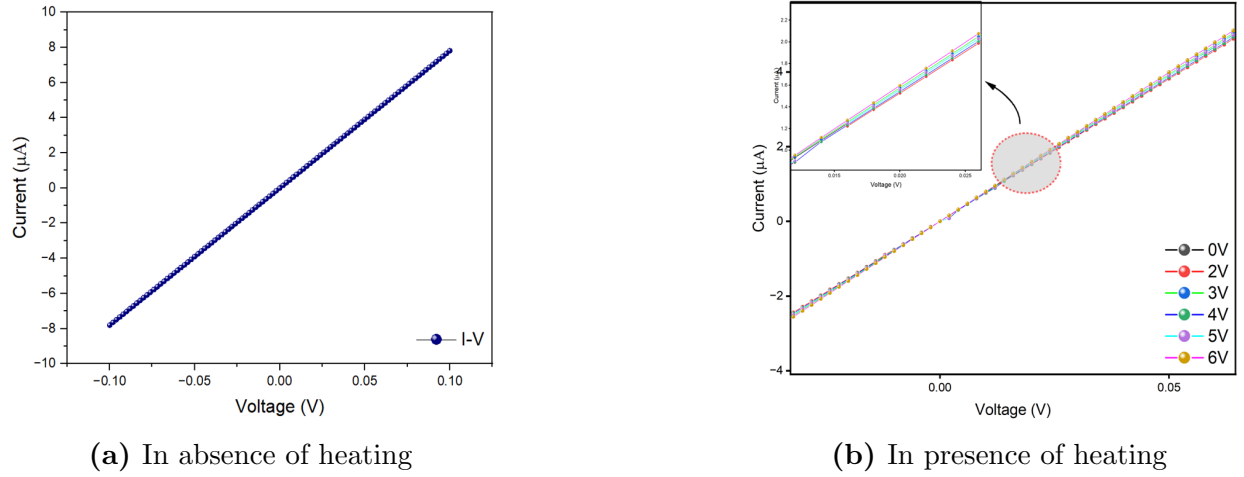


Figure 3.3: I-V Characteristics: a) Linear ohmic IV curve of the Bi_2S_3 thin film without heating. b) Variation in the slope of the IV curve with heating at different temperatures, highlighting the change in resistance of the film.

In order to assess the film's dynamic response to a temperature gradient, we subjected it to various pulsed voltage cycles applied to the Peltier module. A voltage bias of 0.1 V was applied from the source meter, and the time-resolved current characteristics were observed.

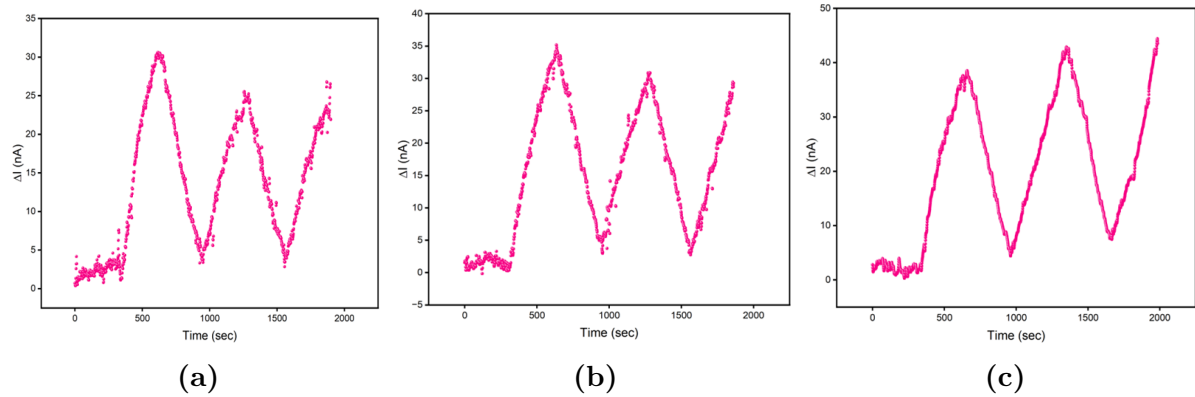


Figure 3.4: Time-Resolved current Characteristics: Plot illustrating the temporal change in current with baseline correction during pulsed Peltier voltage. a) 4V ($T = 66^\circ$) b) 5V ($T = 80^\circ\text{C}$) c) 6V ($T = 90^\circ\text{C}$)

The current characteristics as shown in figure 3.4 show that there is a dynamic change in current (ΔI) at every pulse of Peltier voltage. However, the plot of current versus time exhibited a baseline drift, with the baseline gradually increasing over time instead of remaining

horizontal, which has been corrected. This phenomenon suggests that the current values do not return to their initial levels after each cycle of heating and cooling, even upon returning to room temperature. As a result, a hysteresis effect is observed in the plot, indicating a persistent change in the film’s electrical properties over time.

To measure the Seebeck coefficient, we utilized a Keithley sourcemeter to record the open circuit voltage across the plane while applying Peltier heating at specific voltages. The maximum change in current was taken as the maximum potential difference generated. Additionally, we employed a non-contact laser pyrometer (*micro-epsilon thermoMETER CT-Laser*) to measure the temperature gradient across the film plane. The laser beams marked the measurement spot, ensuring precise temperature measurements. However, due to the relatively large measurement spot size of 0.5 mm, accurately resolving the temperature difference across the film proved challenging. For a Peltier voltage of 3 V, a temperature difference of 2-3°C was observed. Higher voltages resulted in a lesser temperature gradient, likely due to more uniform heat transfer across the entire substrate. Consequently, we chose only two middle-range (2-3 V) voltages to measure the Seebeck coefficient. Using this setup, we determined the thermopower of the thin film sample to be approximately 200-250 $\mu\text{V}/\text{K}$. This indicates the material’s capability to generate a significant potential difference in response to temperature gradients, thereby demonstrating its potential for thermoelectric thin films.

3.2.2 Nanoscale Device

Having established the TE potential of Bi_2S_3 thin films at the microscale level, our research now shifts towards the fabrication and characterization of nanoscale devices. The primary objective of this thesis is to investigate the thermoelectric behavior of Bi_2S_3 thin films at the nano-thickness level. Here the thin film sample or flake has been isolated through mechanical exfoliation of the bulk. The details of the nanoscale device fabrication is detailed in the previous chapter.

For our study, we followed a methodology similar to a recent publication by Chen et al. (2023) on thickness-dependent thermoelectric measurements of WSe_2 to fabricate the device and conduct measurements. We used four-probe resistive measurements to determine the thermopower of the thin film and inferred the local temperature of the flake by monitoring changes in resistance of the contact lines, referencing the temperature coefficient of resistance

(TCR) value from existing literature.

In the calibration process for the temperature gradient at various heater currents, we utilized a device configuration without the transferred flake. This setup allowed us to conduct resistive measurements for each individual contact electrode separately. By examining the IV characteristics of each line, including the heater line, we ensured the continuity of connections throughout the device. For four-probe resistance measurements, we connected the outer pads to the voltage bias terminals and the inner pads to the current sense terminals. This would avoid additional contact resistances and allow us to effectively monitor changes in resistance for both the source and drain lines.

Data were obtained by conducting resistance measurements on the source and drain lines individually, with each line subjected to different heater currents ranging from 0 to 4 V in 1 V increments. However, discrepancies were observed in the initial resistance values between the source and drain lines, which can be attributed to uneven deposition of the gold electrodes. Despite efforts to maintain identical dimensions for both lines, these discrepancies persisted.

It's important to highlight that conducting measurements for the source and drain lines separately rather than simultaneously introduced additional complexities. Fluctuations in ambient conditions and continuous exposure to heating conditions led to variations in transport properties. To avoid this, we manually connected the Keithley Sourcemeter separately to the source and drain lines and performed measurements simultaneously. Due to the use of two source meters, we opted for two-probe measurements instead of four-probe measurements, as the latter were susceptible to fluctuations and exhibited high sensitivity. While the resistance values obtained using two probes were higher than those obtained using four probes due to the inclusion of contact resistances, they demonstrated more stable readings.

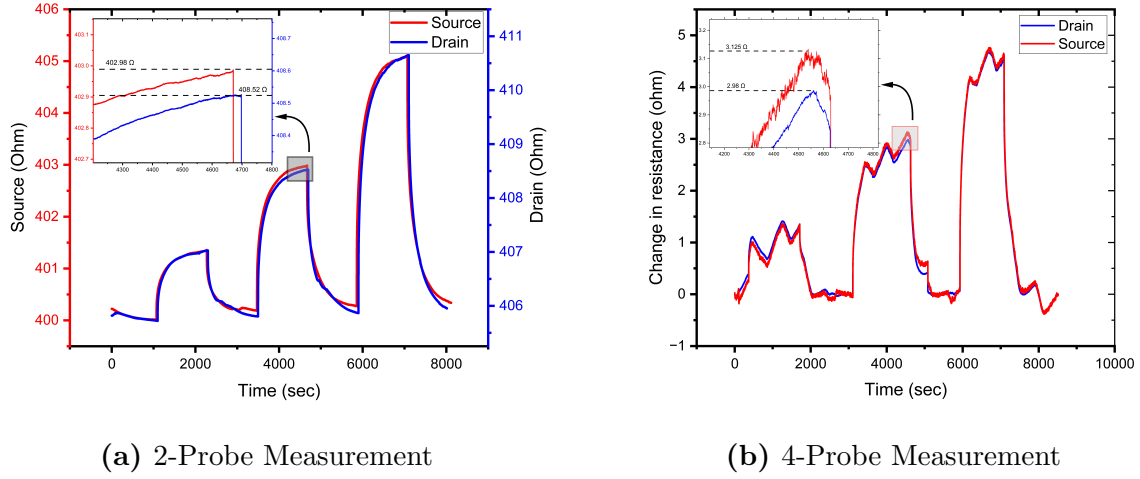


Figure 3.5: Time-resolved resistance plots for the source and drain using **a)** two-probe measurements displayed in a 2-Y plot and **b)** four-probe measurements. The zoomed-in section illustrates the variation in peak heights between the source (red) and drain (blue) plots, indicating the difference in resistance due to heating from one side. Plotted in Origin software.

The observed dynamic fluctuations in resistance, as illustrated in Figure 3.5, directly correspond to variations in heater current, indicating active heating. We deliberately restricted our examination to heater voltages ranging from 0 to 4 volts, as exceeding this range posed potential risks of overheating and damaging the metal lines.

The temperature calculations from the resistance data were based on the Temperature Coefficient of Resistance (TCR) value obtained from the literature for an Au film with a thickness of 50 nm, as reported by Oliva and Lugo 2016 with a TCR value of 0.00324 K^{-1} . Specifically, the temperature differences were measured for the heater voltage of 3V, as this setting exhibited a variance in the peak of the resistance versus time plot, as depicted in Figure 3.5. The difference in peaks corresponding to heater voltages of 1V, 2V, and 4V was relatively insignificant, prompting their exclusion from analysis. We opted to disregard the peak associated with a heater voltage of 1V due to its relatively low magnitude compared to others. The resultant temperature gradient from this measurement under a 3V heater voltage ranged approximately from 0.1 to 0.3 K, as observed through both the 2-probe and 4-probe methods.

To conduct the open-circuit voltage measurement to obtain the Seebeck voltage, we

connected a 2-probe terminal across the two metal lines connected by the flake, with a voltage bias applied. However, during this process, we encountered unexpected challenges. The readings displayed irregularities, with values appearing in Gigaohms and the absence of expected linear IV characteristics in the circuit. Despite efforts to troubleshoot, including repeated attempts and thorough investigation, irregular readings persisted, displaying values in Gigaohms and lacking the anticipated linear IV characteristics. Unfortunately, we were unable to resolve these challenges within the scope of the current study, hindering a conclusive open circuit voltage measurement.

Several potential factors may have contributed to these difficulties. It's plausible that the thin film flake was not adequately positioned on the electrode, resulting in a bridge-like structure due to a height disparity between the electrodes and the flake, thereby compromising electrical contact. Moreover, inconsistencies in the thickness or uniformity of the thin film could have impacted its electrical conductivity, further exacerbating discrepancies. Additionally, impurities or defects within the thin film material might have introduced variations in its electrical properties, compounding the observed inconsistencies.

Chapter 4

Conclusion and Future Works

In conclusion, this thesis has presented a comprehensive investigation into the thermoelectric properties of Bi_2S_3 thin films, with a primary focus on the Seebeck coefficient. Through a combination of microscale and nanoscale device fabrication and characterization, we have demonstrated the potential of Bi_2S_3 thin films as thermoelectric materials.

From the microscale level, we fabricated spray-coated thin film devices and conducted transport property evaluations to ascertain the material's response to temperature gradients. Our findings revealed promising characteristics, including a significant change in current with variations in temperature, indicative of the Seebeck effect.

Moving to the nanoscale, we developed thin-film devices via a top-down approach to synthesize 2D flakes, subsequently integrating them onto micro-fabricated contact electrodes with Bi_2S_3 thin films. Utilizing techniques such as four-probe resistive measurements and time-resolved resistance plots, coupled with the Temperature Coefficient of Resistance (TCR) value of the Au gold contacts, enabled us to accurately determine the temperature gradient across the thin film. Despite encountering challenges, such as irregularities in open-circuit voltage measurements, our efforts shed light on the thermoelectric performance of Bi_2S_3 thin films at the nanoscale.

4.1 Future Works

So far, our focus has been on exploring the Seebeck coefficient of the Bi_2S_3 film. However, there's potential to broaden our investigation to include other transport properties, such as measuring the power factor and, ultimately, determining the figure of merit.

In our future investigations, we will employ various strategies to address the challenges encountered and refine our experimental methodology:

- **Annealing Process:** Introducing annealing steps to reduce the resistance of the channel film by keeping the sample in a furnace at 150-200 °C for 30-60 minutes while flushing with hydrogen (Castellanos-Gómez et al., 2014).
- **Direct Deposition of Electrodes onto Thin Film Flake:** Instead of placing the flake onto pre-deposited electrodes, we'll explore directly overlaying contacts onto the thin film, which can improve the electrical contact and enhance device performance by maximizing contact area.
- **Evaluation of Palladium (Pd) as Contact Pads:** Considering its chemical stability and superior contact properties, Palladium (Pd) will be assessed as an alternative material for contact pads which may address issues related to irregularities in open-circuit voltage measurements.
- **Calibration of Temperature Coefficient of Resistance (TCR):** Despite known TCR values for metal line materials, minor imperfections in fabrication processes may lead to deviations. Hence, independent calibration of TCR for our device will ensure accurate temperature measurements.
- **Accounting for Series Resistance in Thin Film Channel Estimation:** By considering the impact of series resistance introduced by long and thin lines used as source and drain contacts, we aim to estimate the sheet conductance of the thin films. This involves subtracting line resistances and calculating the voltage drop across the thin film to achieve the sheet conductance.
- **Investigating Substrate Impact on Temperature Gradient:** Exploring the adoption of a glass substrate, as opposed to the conventional Si/SiO₂ wafer, offers the potential to minimize vertical heat transfer and reduce lateral temperature drop across the thin

film. This adjustment, as suggested by Chen et al. (2023), could enhance the accuracy of temperature gradient measurements and, thus, the Seebeck coefficient.

- Utilizing a cryostat chamber capable of reaching temperatures as low as 10K, we can conduct measurements to minimize thermal noise and lattice vibration effects.

Furthermore, future research will also focus on investigating the influence of other factors on the thermoelectric performance of Bi_2S_3 thin films, such as the impact of dopants and varying film thicknesses. Also, the application of advanced characterization techniques, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD), will enable detailed analysis of the structural and morphological properties of the thin films which will provide the information about the crystal structure, grain boundaries, and defects, which affect the thermoelectric performance.

In summary, our future research will tackle the challenges we've encountered, explore different ways to make and study these devices and deepen our understanding of how Bi_2S_3 thin films behave thermoelectrically. By doing this, we hope to create better thermoelectric materials that can be used to generate energy, recover waste heat, and manage temperatures more effectively.

Appendix A

Appendix

A.1 Microscale Device Fabrication and Packaging

The Microscale device comprises the substrate containing the spray-coated film and the heater, which is represented by the Peltier module positioned perpendicular to the substrate as shown in figure A.1. Gold pads on the substrate are connected to a Printed Circuit Board (PCB) via wire bonding for electrical connectivity.

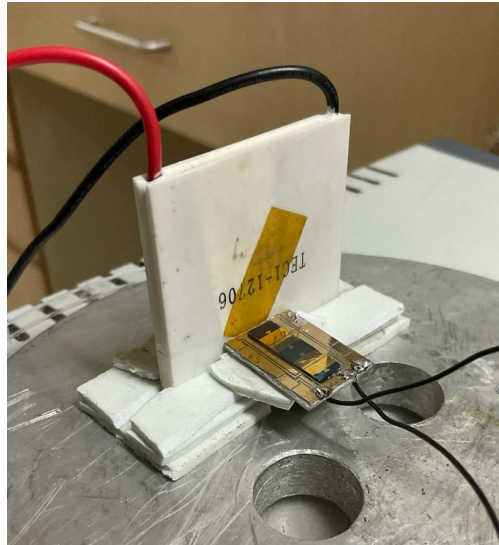


Figure A.1: Microscale Device Setup: Photograph depicting the setup of the microscale device with the Peltier module positioned perpendicular to the substrate.

The Peltier module is connected to the DC supply to generate heat, with the substrate positioned on the heated side (indicated by heat-resistant tape). The leads from two sides of the film substrate are extended and connected to a Keithley SourceMeter for electrical measurements, as described in the Transport Properties and Measurements section.

A.2 COMSOL Simulation of the Nanoscale Device

In this section, we present the details of the COMSOL Multiphysics simulations conducted to analyze the performance and behavior of the nanoscale device under various operating conditions. We drew inspiration from the research conducted by Chen et al. 2023 as a basis for our work.

Our model closely matches the dimensions of the experimental substrate, with a slight reduction in substrate thickness for better visualization. While our simulations used a substrate thickness of 0.1 mm, the experimental and full-scale simulation scenarios maintained a thickness of 0.5 mm.

To study heat transfer across the substrate, we utilized the thermal finite element method. This method allowed us to simulate the thermal behavior of our device under different conditions, providing insights into heat flow patterns and temperature distributions.

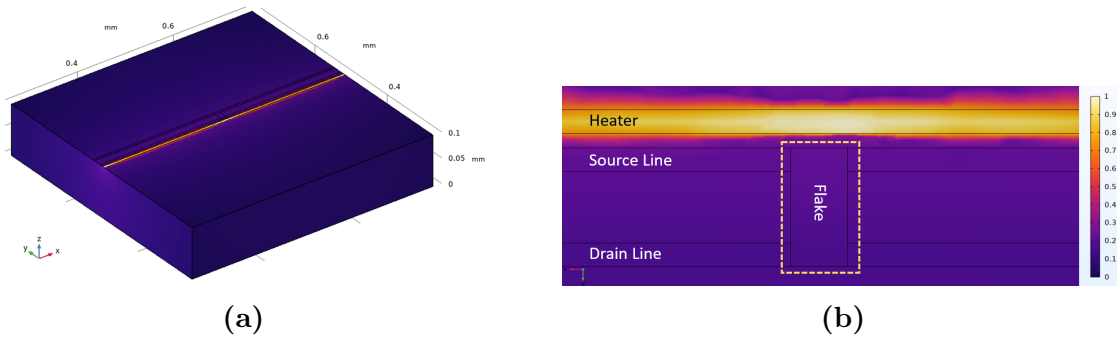


Figure A.2: Snapshot of the heat transfer simulation illustrating the Device Under Test (DUT) on a Si/SiO₂ substrate. The temperature distribution is represented using a heat-camera color table and normalized relative to the maximum temperature, T_H , at the heater. **a)** Default 3D perspective **b)** Top view showing the heat flow across the metal lines with the flake atop.

In order to evaluate the significance of substrate selection in thermal design, we conducted simulations using two different substrates: the conventional Si/SiO₂ substrate with a 300 nm SiO₂ layer and glass substrate consisting solely of SiO₂. Both substrates featured identical metal electrodes and heater temperatures to ensure consistency across experiments.

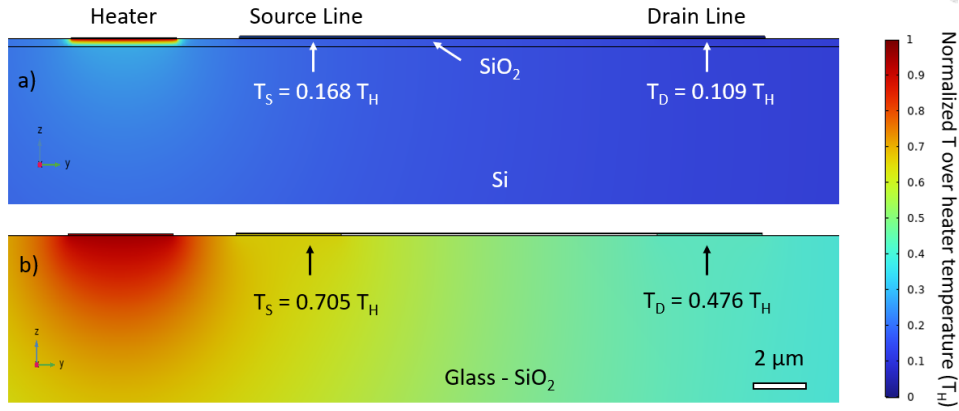


Figure A.3: Comparison of heat transfer simulations with (a) typical Si/SiO₂ substrate (300 nm SiO₂) and (b) Glass (SiO₂) substrate. The color scheme represents temperature variation, displayed using a Rainbow color table. The substrate thickness has been reduced for visualization purposes.

Due to the highly conductive nature of Si ($\kappa_{Si} = 130 \text{ W/m/K}$), the temperature across the substrate rapidly equilibrates with ambient conditions over a short distance, evident in Figure A.3a. Acting as a thermal ground, this results in substantially lower temperatures for both the source (T_S) and drain line (T_D) compared to the heater temperature (T_H). Consequently, the temperature difference ($T_S - T_D = 0.059 T_H$) is also minimized. Conversely, when using glass as the substrate, characterized by significantly lower thermal conductivity ($\kappa_{glass} = 1.4 \text{ W/m/K}$), there is a notable reduction in the temperature drop across the source and drain lines ($T_S - T_D = 0.23 T_H$) as shown in Figure A.3b.

Bibliography

- Cahill, D. G., Watson, S. K., and Pohl, R. W. (1992). Lower limit to the thermal conductivity of disordered crystals. *Physical review*, 46(10):6131–6140.
- Castellanos-Gómez, A., Buscema, M., Molenaar, R., Singh, V., Janssen, L., Van Der Zant, H. S. J., and Steele, G. A. (2014). Deterministic transfer of two-dimensional materials by all-dry viscoelastic stamping. *2D Materials*, 1(1):011002.
- Ceballos, F., Bellus, M. Z., Chiu, H.-Y., and Zhao, H. (2014). Ultrafast charge separation and indirect exciton formation in a mos2–mose2 van der waals heterostructure. *ACS nano*, 8(12):12717–12724.
- Chen, L., Liu, R., and Shi, X. (2020). *Thermoelectric materials and devices*. Elsevier.
- Chen, V., Lee, H. R., Köroğlu, , McClellan, C. J., Daus, A., and Pop, E. (2023). Ambipolar Thickness-Dependent thermoelectric measurements of WSe2. *Nano Letters*, 23(10):4095–4100.
- Chen, Z., Han, G., Yang, L., Cheng, L., and Zou, J. (2012). Nanostructured thermoelectric materials: Current research and future challenge. *Progress in Natural Science: Materials International*, 22(6):535–549.
- EI (2023). Statistical review of World Energy.
- Faleev, S. V. and Léonard, F. (2008). Theory of enhancement of thermoelectric properties of materials with nanoinclusions. *Physical Review B*, 77(21).
- Ge, Z., Qin, P., He, D., Chong, X., Feng, D., Ji, Y.-H., Feng, J., and He, J. (2017). Highly enhanced thermoelectric properties of Bi/Bi₂S₃ nanocomposites. *ACS Applied Materials Interfaces*, 9(5):4828–4834.

- Goldsmid, H. J. (2009). *Introduction to thermoelectricity*. Springer.
- Han, C., Li, Z., and Dou, S. X. (2014). Recent progress in thermoelectric materials. *Chinese Science Bulletin*, 59(18):2073–2091.
- Heremans, J. P., Jovovic, V., Toberer, E. S., Saramat, A., Kurosaki, K., Charoenphakdee, A., Yamanaka, S., and Snyder, G. J. (2008). Enhancement of thermoelectric efficiency in PBTE by distortion of the electronic density of states. *Science*, 321(5888):554–557.
- Hicks, L. D. and Dresselhaus, M. S. (1993). Effect of quantum-well structures on the thermoelectric figure of merit. *Physical review*, 47(19):12727–12731.
- Hicks, L. D., Harman, T. C., Sun, X., and Dresselhaus, M. S. (1996). Experimental study of the effect of quantum-well structures on the thermoelectric figure of merit. *Physical review*, 53(16):R10493–R10496.
- Huang, W., Xing, C., Wang, Y., Li, Z., Wu, L., Ma, D., Dai, X., Xiang, Y., Li, J., Fan, D., and Zhang, H. (2018). Facile fabrication and characterization of two-dimensional bismuth(iii) sulfide nanosheets for high-performance photodetector applications under ambient conditions. *Nanoscale*, 10(5):2404–2412.
- Ioffe, A. F., Stil’bans, L., Iordanishvili, E. K., Stavitskaya, T. S., Gelbtuch, A., and Vineyard, G. H. (1959). Semiconductor thermoelements and thermoelectric cooling. *Physics Today*, 12(5):42.
- Ji, W., Yu, H., Zhou, D., Li, X., Fan, X., Zhang, Y., Hong-Yan, M., and Jia, X. (2023). Cation and anion doping to enhance thermoelectric performance of Bi₂S₃. *Journal of Solid State Chemistry*, 322:123990.
- Kim, H.-S., Heinz, N. A., Gibbs, Z. M., Tang, Y., Kang, S. D., and Snyder, G. J. (2017). High thermoelectric performance in (Bi_{0.25}Sb_{0.75})₂Te₃ due to band convergence and improved by carrier concentration control. *Materials Today*, 20(8):452–459.
- Kim, S. I., Lee, K. H., Mun, H. A., Kim, H. S., Hwang, S. W., Roh, J. W., Yang, D. J., Shin, W. H., Li, X. S., Lee, Y. H., Snyder, G. J., and Kim, S. W. (2015). Dense dislocation arrays embedded in grain boundaries for high-performance bulk thermoelectrics. *Science*, 348(6230):109–114.

- Koga, T., Cronin, S. B., Dresselhaus, M. S., Liu, J. L., and Wang, K. L. (2000). Experimental proof-of-principle investigation of enhanced Z3DT in (001) oriented Si/Ge superlattices. *Applied Physics Letters*, 77(10):1490–1492.
- Koh, Y. K., Bae, M., Cahill, D. G., and Pop, E. (2010). Reliably Counting Atomic Planes of Few-Layer Graphene (n gt; 4). *ACS Nano*, 5(1):269–274.
- Kudelski, A. (2008). Analytical applications of Raman spectroscopy. *Talanta*, 76(1):1–8.
- Lan, Y., Minnich, A. J., Chen, G., and Ren, Z. (2010). Enhancement of thermoelectric Figure-of-Merit by a bulk nanostructuring approach. *Advanced Functional Materials*, 20(3):357–376.
- Lee, M.-J., Ahn, J., Sung, J. H., Heo, H., Jeon, S. G., Lee, W., Song, J. Y., Hong, K., Choi, B., Lee, S.-H., and Jo, M. (2016). Thermoelectric materials by using two-dimensional materials with negative correlation between electrical and thermal conductivity. *Nature Communications*, 7(1).
- Li, S. L., Miyazaki, H., Song, H., Kuramochi, H., Nakaharai, S., and Tsukagoshi, K. (2012). Quantitative Raman spectrum and reliable thickness identification for atomic layers on insulating substrates. *ACS Nano*, 6(8):7381–7388.
- Li, X., Qiao, X., Han, W., Lü, Y., Tan, Q., Liu, X.-L., and Tan, P. (2015). Layer number identification of intrinsic and defective multilayered graphenes up to 100 layers by the Raman mode intensity from substrates. *Nanoscale*, 7(17):8135–8141.
- Liufu, S., Chen, L., Qin, Y., and Wang, C.-F. (2007). Assembly of one-dimensional nanorods into Bi₂S₃ films with enhanced thermoelectric transport properties. *Applied Physics Letters*, 90(11).
- Malard, L. M., Pimenta, M. A., Dresselhaus, G., and Dresselhaus, M. S. (2009). Raman spectroscopy in graphene. *Physics Reports*, 473(5-6):51–87.
- Meitl, M. A., Zhu, Z.-T., Kumar, V., Lee, K. J., Feng, X., Huang, Y. Y., Adesida, I., Nuzzo, R. G., and Rogers, J. A. (2006). Transfer printing by kinetic control of adhesion to an elastomeric stamp. *Nature materials*, 5(1):33–38.
- Messalea, K. A., Zavabeti, A., Mohiuddin, M., Syed, N., Jannat, A., Atkin, P., Ahmed, T., Walia, S., McConville, C. F., Kalantar-Zadeh, K., et al. (2020). Two-step synthesis

-
- of large-area 2d bi₂s₃ nanosheets featuring high in-plane anisotropy. *Advanced Materials Interfaces*, 7(22):2001131.
- Minnich, A. J., Dresselhaus, M. S., Ren, Z., and Chen, G. (2009). Bulk nanostructured thermoelectric materials: current research and future prospects. *Energy and Environmental Science*, 2(5):466.
- Mott, N. F. and Jones, H. (1958). *The theory of the properties of metals and alloys*. Courier Dover Publications.
- Mulla, R., Kiani, S., White, A. O., Dunnill, C. W., and Barron, A. R. (2023). Enhanced thermoelectricity in Bi-sprayed bismuth sulphide particles. *Materials Science in Semiconductor Processing*, 162:107528.
- Nandi, S. and Misra, A. (2019). Spray coating of Two-Dimensional suspended film of vanadium Oxide-Coated carbon nanotubes for fabrication of a large volume infrared bolometer. *ACS Applied Materials Interfaces*, 12(1):1315–1321.
- Ni, Z., Wang, H., Kasim, J., Fan, H., Yu, T., Wu, Y., Feng, Y. P., and Shen, Z. (2007). Graphene thickness determination using reflection and contrast spectroscopy. *Nano Letters*, 7(9):2758–2763.
- Nolas, G. S., Slack, G. A., Morelli, D. T., Tritt, T. M., and Ehrlich, A. C. (1996). The effect of rare-earth filling on the lattice thermal conductivity of skutterudites. *Journal of Applied Physics*, 79(8):4002–4008.
- Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D.-e., Zhang, Y., Dubonos, S. V., Grigorieva, I. V., and Firsov, A. A. (2004). Electric field effect in atomically thin carbon films. *science*, 306(5696):666–669.
- Novoselov, K. S., Jiang, D., Schedin, F., Booth, T., Khotkevich, V., Morozov, S., and Geim, A. K. (2005). Two-dimensional atomic crystals. *Proceedings of the National Academy of Sciences*, 102(30):10451–10453.
- Oliva, A. and Lugo, J. E. (2016). Measurement of the Temperature Coefficient of Resistance in Metallic Films with Nano-thickness. *International Journal of Thermophysics*, 37(3).
- Patil, P. S. (1999). Versatility of chemical spray pyrolysis technique. *Materials Chemistry and physics*, 59(3):185–198.

- Ravich, Y. I., Efimova, B. A., and Tamarchenko, V. (1971). Scattering of current carriers and transport phenomena in lead chalcogenides II. experiment. *physica status solidi (b) basic solid state physics*, 43(2):453–469.
- Richmond, P. (1966). The Peltier effect. *Physics Education*, 1(3):145–153.
- Rowe, D. B. (1974). Theoretical optimization of the thermoelectric figure of merit of heavily doped hot-pressed germanium-silicon alloys. *Journal of Physics D: Applied Physics*, 7(13):1843–1846.
- Rowe, D. M. (2018). *Thermoelectrics handbook: macro to nano*. CRC press.
- Seebeck, T. J. (1826). Ueber die magnetische Polarisierung der Metalle und Erze durch Temperatur-Differenz. *Annalen der Physik*, 82(2):133–160.
- Shi, X., Zou, J., and Chen, H. (2020). Advanced thermoelectric design: from materials and structures to devices. *Chemical Reviews*, 120(15):7399–7515.
- Team, S. (2023). Wire bonding: an efficient interconnection technique.
- Thomson, W. (1857). 4. on a mechanical theory of thermo-electric currents. *Proceedings of the Royal society of Edinburgh*, 3:91–98.
- Trentelman, K. (2009). A note on the characterization of bismuth black by Raman microspectroscopy. *Journal of Raman Spectroscopy*, 40(5):585–589.
- Tripathi, R. and Misra, A. (2021). A novel approach towards molecular memory device in gate tunable structure of mos 2-graphene. *Nano Research*, 14:177–184.
- U.S. Energy Information Administration (EIA) (2023). International Energy Outlook 2023: Analysis and Projections to 2050. <https://www.eia.gov/outlooks/ieo/>.
- Wiedemann, G. and Franz, R. (1853). Relative conductivity of solids. *Ann. Phys. Chem*, 89:497–531.
- Yang, L., Chen, Z., Dargusch, M. S., and Zou, J. (2017). High performance thermoelectric materials: progress and their applications. *Advanced Energy Materials*, 8(6).
- Yu, Y., Cagnoni, M., Cojocaru-Mirédin, O., and Wuttig, M. (2019). Chalcogenide thermoelectrics empowered by an unconventional bonding mechanism. *Advanced Functional Materials*, 30(8).

- Yuan, P., Wang, R., Tan, H., Wang, T., and Wang, X. (2017). Energy Transport State resolved Raman for probing interface energy transport and hot carrier diffusion in Few-Layered MOS₂. *ACS Photonics*, 4(12):3115–3129.
- Yue, Y. and Wang, X. (2012). Nanoscale thermal probing. *Nano Reviews*, 3(1):11586.
- Zhu, T., Liu, Y., Fu, C., Heremans, J. P., Snyder, G. J., and Zhao, X. (2017). Compromise and synergy in High-Efficiency Thermoelectric Materials. *Advanced Materials*, 29(14).
- Zumeta-Dubé, I., Ruiz-Ruiz, V.-F., Díaz, D. D., Rodil, S., and Zeinert, A. (2014). TiO₂Sensitization with Bi₂S₃Quantum Dots: The Inconvenience of Sodium Ions in the Deposition Procedure. *The Journal of Physical Chemistry C*, 118(22):11495–11504.