



國立臺灣大學理學院物理學系

博士論文

Department of Physics

College of Science

National Taiwan University

Doctoral Dissertation

$\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ 薄膜之熱電性質研究和

Sb_2Te_3 奈米片的拓樸超導性質

Thermoelectric Properties in $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ Thin Film and
Topological Superconductivity in Sb_2Te_3 Nanoflakes

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中華民國 113 年 7 月

July, 2024

誌謝



博士學位一直是我夢寐以求的目標。從小我並不是特別擅長讀書，但在大學時期，有幸進入中央研究院物理所陳洋元老師的實驗室進行專題研究，這段經歷開啟了我對實驗物理的熱愛。非常感謝陳洋元老師多年來的悉心栽培，從大學、碩士、研究助理到博士班，這十多年的學術旅程，我始終有幸在老師的指導下學習。儘管我不是老師最優秀的學生，老師依然耐心的指導我，無論是在學業還是生活上，這段學習旅程對我的人生意義深遠，在此，我由衷地向老師致謝。

在這段漫長的博士班旅程中，我得到了許多貴人的幫助。感謝陳正龍博士、歐敏男博士、李秉中博士和洪慈蓮博士，在實驗和儀器操作上不吝指導。此外，也感謝在這段旅程中一同奮鬥的同學和同事——佳華、世勛、凡芸、RK、晉毅，感謝你們在實驗、討論及玩耍中的陪伴。還有許多學弟妹——益嘉、凱威、Ava、嵐熙、子由，以及眾多好朋友——孫穎、彥舒、其辰、若辰、昱婷、驅，因為有你們的陪伴，這段旅程變得更加豐富和充實，無論是喜悅還是挫折，都讓我不孤單。特別感謝我的妻子怡伶，我們在我博士班第二年時相識，這些年來妳一直耐心等待著我完成學業。如今，我終於可以對妳說：「我畢業了！」

感謝台大的指導教授黃斯衍老師，雖然我們的交流並不多，但您溫文儒雅的風範讓我深受啟發，您總是提醒我專注於當下最重要的事情，並在我偏離軌道時拉我一把，對此我深表感謝。

最後，我要感謝我的父母，看著我頑皮成長，即使我不愛讀書，依然鼓勵我選擇普通高中，當我決定攻讀博士學位時，你們也沒有反對，一直是我堅實的後盾。還有我最愛的外婆，終於可以邀請您參加我的畢業典禮了。

感謝所有愛我的人，你們的陪伴是我完成這段旅程的最大動力。

中文摘要



本博士論文包涵兩個研究主題和一個熱電特性量測技術補充資料。兩個研究主題集中於低維熱電和拓撲超導特性的研究，前者研究 $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ 薄膜，後者則研究 Sb_2Te_3 奈米片，熱電特性測量技術用於測量單腿 AgSbTe_2 裝置的熱電性能。 $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ 薄膜的研究，主要是通過調整電子和聲子的傳輸特性來提高 ZT 值。使用 RF 濺射法製備了一系列厚度分別為 0.125、0.25、0.5 和 1 微米的 $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ 薄膜，其微觀結構分析顯示薄膜的生長形態與薄膜厚度有高度相關。值得注意的是，0.5 微米厚的薄膜在 400 K 時功率因子達到了 $18.1 \mu\text{Wcm}^{-1}\text{K}^{-2}$ ，並具有低至 $0.3 \text{ Wm}^{-1}\text{K}^{-1}$ 的熱傳導率，實現了接近室溫的最大 ZT 值 1.86。

Sb_2Te_3 奈米片的研究，在氮化矽基板上製備了一系列厚度為 5 到 27 奈米的超薄薄膜，此研究與作者周柏豪、牟中瑜教授合作，根據其提出的理論及計算，此薄型拓撲絕緣體表面電子間的相互配對形成的新型拓撲超導體。本研究顯示， Sb_2Te_3 奈米片在 a-b 平面上是通過層與層範德瓦力結合的。我們實驗結果表明，由於表面狄拉克錐間耦合而形成的配對對稱性，是由自 $p_x + ip_y$ 配對主導，形成了一類新的拓撲超導體。

第三部份為補充資料，熱電裝置效率的研究，為了直接測量熱電材料的輸出功率以獲得效率，最可靠的方法是直接測量其輸出功率，而不是藉由測量各別的熱電參數計算 ZT 值。本研究利用四點探針法測量單腿 AgSbTe_2 的熱電轉換效率。這種四點探針法能有效減少測量過程中線阻和接觸電阻的影響，此研究在 156 K 的溫差下，樣品測量出 6.4 mW 的輸出功率，且有 2.1 % 的轉換效率，與傳統單獨量測熱電參數計算的 ZT 值一致。

綜合以上研究，本論文為高性能熱電系統的設計與製造提供了重要的科學見解和技術突破。透過這些先進材料的開發，我們朝著實現高效能的熱電轉換技術邁進，為未來可持續能源解決方案的實現奠定了堅實的基礎。此外本研究展示了超薄單晶 Sb_2Te_3 奈米薄片的新型拓撲超導性，提供了拓撲材料研究的新方向。

關鍵字：熱電材料、熱電裝置、薄膜、奈米片、拓撲材料

ABSTRACT

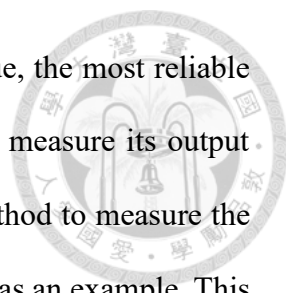


The doctoral thesis encompasses two thematic research topics and one supplementary thermoelectric (TE) characterization technique. The two research topics focus on the study of low-dimensional thermoelectric and topological superconducting properties. The former is on thermoelectric $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ thin film, and the latter is on Sb_2Te_3 nanoflakes. The thermoelectric characterization technique is used to measure the thermoelectric performance of a single-leg AgSbTe_2 device.

The study on thermoelectric $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ thin film aims to examine the ZT enhancement through the decoupling of the transport properties of electrons and phonons. A series of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ thin films with thicknesses of 0.125, 0.25, 0.5, and 1 μm were fabricated by RF sputtering. Detailed microstructural analysis revealed that the growth morphology of the films is highly correlated with the film thickness. Notably, the 0.5 μm film achieved a power factor of $18.1 \mu\text{Wcm}^{-1}\text{K}^{-2}$ at 400 K and a thermal conductivity as low as $0.3 \text{ Wm}^{-1}\text{K}^{-1}$, resulting in a maximum figure of merit ZT of 1.86 near room temperature.

In the study of Sb_2Te_3 nanoflakes, a series of ultrathin films grown on silicon nitride substrates with thicknesses ranging from 5 to 27 nm were fabricated. This research was conducted in collaboration with Po-Hao Chou, Chung-Yu Mou, et al., based on their proposed theory and calculations. A new class of topological superconductivity was formed by inter-surface pairing of surface electrons in the thin topological insulators. This study demonstrated that Sb_2Te_3 nanosheets are bonded through van der Waals forces in the a-b planes, layer-by-layer. Our results indicate that the pairing symmetry due to the coupling of inter-surface Dirac cones is unambiguously dominated by the spinful $p_x + ip_y$ pairing and forms a new class of topological superconductors.

This supplementary information pertains to the study of thermoelectric device efficiency.



Instead of measuring separate TE properties to calculate the ZT value, the most reliable way to characterize the performance of a TE material is to directly measure its output power to gain efficiency. The study utilized the four-point probe method to measure the thermoelectric conversion efficiency on a single-leg AgSbTe₂ device as an example. This four-point probe method can effectively reduce the influence of line and contact resistance during measurements. At a temperature difference of 156 K, the sample exhibited a power output of 6.4 mW, corresponding to a conversion efficiency of 2.1%, which is consistent with the ZT value obtained from conventional individual TE parameters.

In summary, this thesis provides important scientific insights and technological breakthroughs for the design and fabrication of low-dimensional high-performance thermoelectric systems. Through the development of these advanced materials, we are moving towards achieving high-efficiency thermoelectric performance technologies, laying a solid foundation for the realization of future sustainable energy solutions. Additionally, this research demonstrates a new class of topological superconductivity in ultrathin single-crystal Sb₂Te₃ nanoflakes, offering a new direction for topological material studies.

Keywords: Thermoelectric materials, Thermoelectric devices, Thin films, Nanoflakes, Topological materials.

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Part I. Enhancement of ZT in $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ Thin Film through Lattice Orientation Management

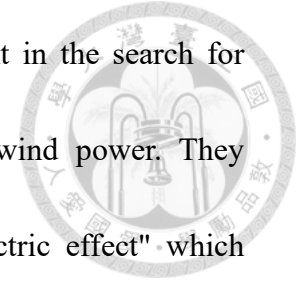
Chapter 1 Introduction of Thermoelectricity



1.1 Thermoelectric Fundamentals

Energy is crucial for humanity and drives rapid industrial and technological growth, promoting development in all areas. However, global warming has become the most urgent concern, and energy calamity is worsening because of the combusting fossil fuels. Increased energy use and heavy reliance on non-renewable fossil fuels drive the economy and sustain daily life, leading to an excessive imbalance between supply and demand. This imbalance has caused an energy crisis, with global energy usage expected to treble by 2050 despite daily increases. As a result, it is essential to increase global energy production rates while also considering the various environmental problems the world is facing. Studies have demonstrated the need for alternative energy sources and innovative technologies that use our current supply of fossil fuels as efficiently as possible. This need has initiated extensive research for the alternate energy sources and various waste heat conversion technology. Thermoelectric materials have emerged as a promising solution, capable of transforming industrial waste heat into consumable energy and vice-versa. This cost-effective and environmentally friendly energy-conversion technology operates in a solid-state manner, without moving parts or chemical interactions, offering a long lifespan of dependable, maintenance-free

operation. Thermoelectric materials [1-5] are particularly relevant in the search for alternative renewable energy sources such as solar cells and wind power. They encompass three distinct effects, together known as "thermoelectric effect" which consists of three parameters called Seebeck, the Peltier, and the Thomson effect.



1.2 Basic Concepts of Thermoelectric

1.2.1 The Seebeck Effect

The Seebeck Effect [6] occurs when a temperature difference between two different conductors or semiconductors materials causes an electric potential. This phenomenon happens when temperature dissimilarities induce charge carriers in materials (such as electrons or holes) diffuses from the hot to the cold side, resulting a voltage.

The Seebeck coefficient (S) is defined as ratio of the generated voltage differential to the temperature gradient across the material. Mathematically, it is written as:

$$S = -\frac{\Delta V}{\Delta T} = -\frac{V_h - V_c}{T_h - T_c} \quad (1)$$

Here S is Seebeck coefficient, typically calculated in volts per kelvin (V/K). ΔV is the voltage difference generated between the two points. ΔT is the temperature difference between those two points. The Seebeck coefficient is a measure of the magnitude of an

induced thermoelectric voltage in response to a temperature difference across a material.

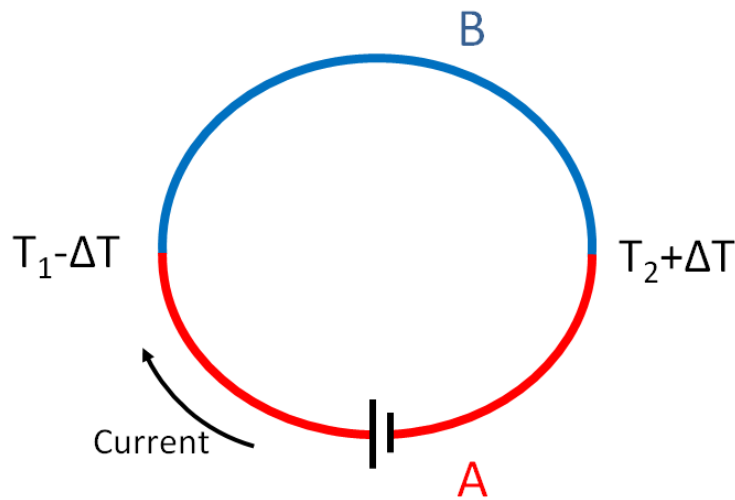


Fig.I.1. 1 The Seebeck effect

1.2.2 The Peltier Effect

Peltier Effect [7] is a thermoelectric phenomenon was caused by the heating or cooling at the junction of two dissimilar conductors or semiconductor material when an electric current flows across them. Electric current (I) runs from one conductor A to another B, the junction absorbs or releases heat, depending on the current's direction and the materials involved. This effect can be described by the following equation:

$$Q = (\pi_A - \pi_B)I \quad (2)$$

Where Q is the rate of heat generation or absorption at the junction and π_A and π_B are the Peltier coefficients of conductors A and B, respectively. The Peltier coefficient represents the amount of heat carried per unit charge by an electron or hole in a material.

I is the electric current flowing from conductor A to conductor B.

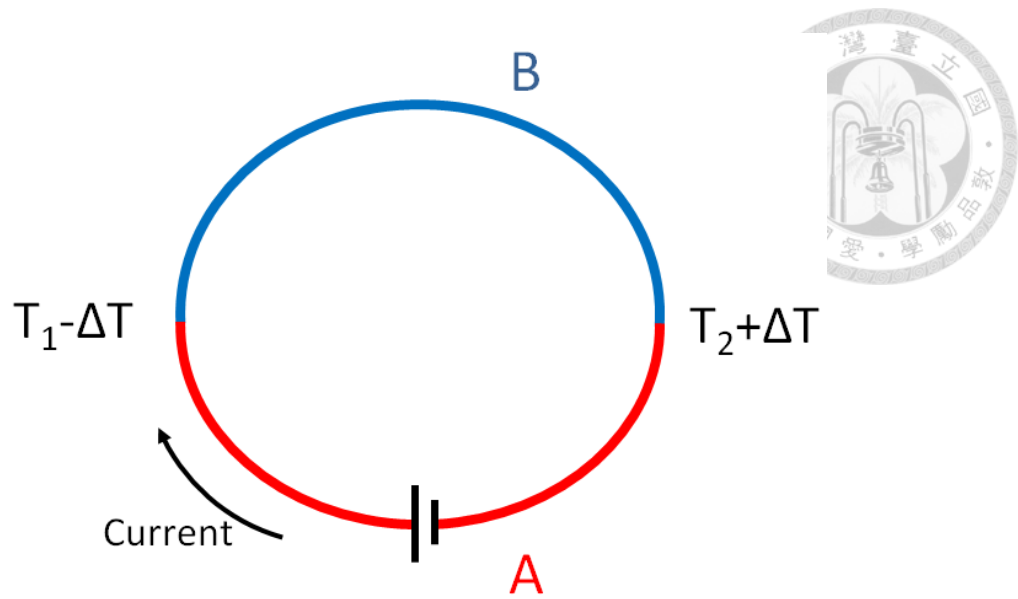


Fig.I.1. 2 The Peltier effect

1.2.3 The Thomson Effect

Thomson Effect is a thermoelectric phenomenon observed in a homogeneous conductor carrying an electric current and subject to a temperature gradient. Contrasting to Seebeck and Peltier effects involve thermocouples (junctions of two different materials), whereas Thomson Effect occurs within a one material. It describes the absorption or release of heat along the length of the conductor due to the presence of both an electric current and a temperature gradient. When an electric current passes through a conductor with a temperature gradient, heat is either absorbed or released depending on the current's direction relative to the temperature difference.

$$Q = \rho J^2 - \mu J \frac{\Delta T}{\Delta X} \quad (3)$$

ρ is the electrical resistivity of the conductor. J is the current density. $\Delta T/\Delta X$ is the

temperature gradient along the conductor. μ is the Thomson coefficient of the material.

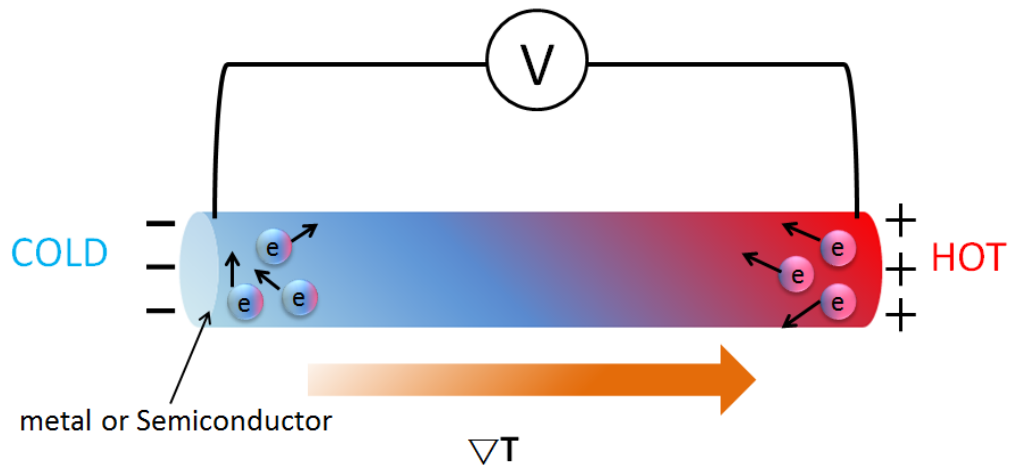


Fig.I.1. 3 The Thomson effect

1.2.4 The Figure of Merit (ZT)

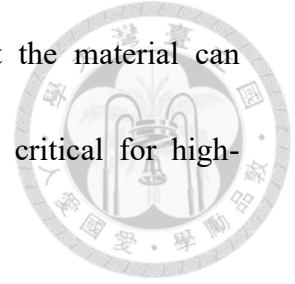
The figure of merit [1,8,9] is a dimensionless factor (ZT) used to characterize the performance of thermoelectric materials. This is a crucial indicator of a material's efficiency in converting heat energy into electrical energy and vice-versa. ZT is defined as below equation:

$$ZT = \frac{S^2 \sigma T}{\kappa} = \frac{S^2 T}{\rho \kappa} \quad (4)$$

Here S is the Seebeck coefficient, ρ is the electrical resistivity, representing the opposition to the flow of electric current in a material, T is absolute temperature at which material was operating. κ is the thermal conductivity.

The term S^2/ρ is called as power factor. It represents the material's ability to generate

power per unit volume. High power factor values indicate that the material can efficiently convert thermal energy to electrical energy, which is critical for high-performance thermoelectric devices.



1.2.5 The Thermoelectric Devices

Thermoelectric devices [1] are typically composed of 2 distinctive types of semiconductor material:

P-type materials: The primary charge carriers in these materials are holes (positive charges). When a temperature difference exists, the hole's interchange from the hot region to the cold region, generating an electromotive force.

N-type materials: The primary charge carriers in these materials are electrons (negative charges). When a temperature difference exists, the electrons travel from the hot side to the cold side, generating an electromotive force.

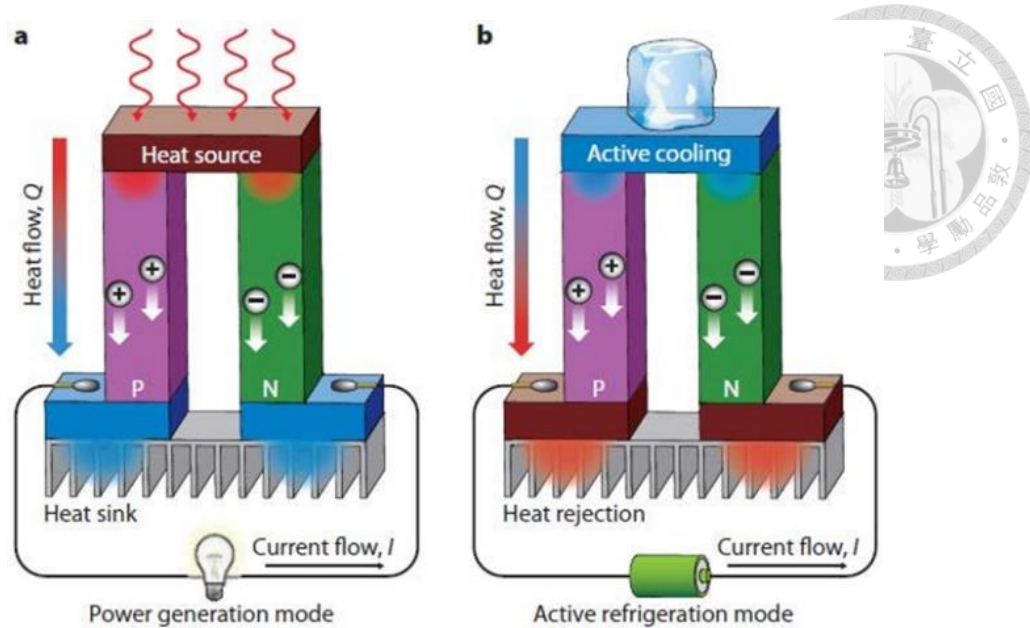


Fig.I.1. 4 Schematic representation of a thermoelectric module for (a) power generation and active refrigerator mode

Thermoelectric generators [4-8] utilize the Seebeck to convert heat energy into electrical energy. When one end of the P-type and N-type materials is at a high temperature and the other end is at a low temperature, the charge carriers in both materials move, creating a voltage. This voltage can be used to drive an electric current, thereby generating electricity.

1.2.6 The Thermoelectric Efficiency

Thermoelectric efficiency is parameter is used to measure the performance of thermoelectric material and devices, depending on material's (ZT) and operating

conditions. By improving materials, optimizing thermal management, and enhancing device design, thermoelectric efficiency can be significantly increased, leading to efficient energy utilization and sustainable development. The efficiency [1] can be calculated by the below formula:

$$\eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + zT} - 1}{\sqrt{1 + zT} + \frac{T_C}{T_H}} \quad (5)$$

η is the thermoelectric efficiency. T_H is the absolute T of the hot end. T_C

is the absolute T at the cold end.

1.3 Factors involved in Thermoelectric

From section 1.2.4, it is known that thermoelectric performance is influenced by several key factors. Understanding these factors is crucial for improving the efficiency of thermoelectric energy conversion. By optimizing the resistivity, Seebeck, and thermal conductivity, efficiency of thermoelectric materials and devices can be significantly enhanced.

1.3.1 The Electrical Conductivity

Electrical conductivity is a key property of materials that quantifies their ability to conduct electric current. Electrical conductivity was denoted by the symbol (σ) and is

measured in (S/m). Conductivity was inverse to the electrical resistivity (ρ), which measures a material's opposition to the flow of electric current.

$$s = \frac{1}{r} = nem \quad (6)$$

where n , e , and μ are the charge carrier concentration (m^{-3}), electrical charge, and mobility ($m^2V^{-1}s^{-1}$) respectively. The charge carrier concentration represents the number of charge carriers (electrons or holes) per unit volume. A higher carrier density generally leads to higher conductivity.

1.3.2 The Seebeck Coefficient

The Seebeck coefficient is a key parameter in thermoelectric materials that quantifies the voltage generated in response to a temperature gradient across a material. Qualitatively, it can be defined as the entropy per charge carrier, indicating the amount of heat carried with each unit charge, thus linking thermal and electrical currents. The Seebeck coefficient can be mathematically represented using the Mott formula after detailed theoretical treatment:

$$S = \frac{p^2 K_B^2}{3e} T \left\{ \frac{d \ln(s(E))}{dE} \right\}_{E=E_F} \quad (7)$$

where K_B is the Boltzmann constant, e is the elementary charge, T is the absolute temperature, and E_F is the Fermi energy.

The Seebeck coefficient S for metals and degenerate semiconductors is represented by the equation:

$$S = \frac{8p^2 K_B^2}{3eh^2} m^* T \left(\frac{p}{3n} \right)^{\frac{2}{3}} \quad (8)$$

where h is Planck's constant, and m^* is the effective mass of the charge carriers.

The m^* of the charge carriers is a crucial component that affects the Seebeck coefficient.

Relatively large effective masses result in a high Seebeck coefficient but also lead to lower electrical conductivity. This indicates a trade-off between achieving a high Seebeck coefficient and maintaining good electrical conductivity.

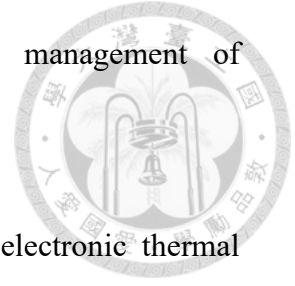
1.3.3 The Thermal Conductivity

Thermal conductivity (κ) is a key property of materials that measures their ability to conduct heat. In generally thermoelectric materials κ is composed of two main components: lattice (κ_l), which is due to the vibrations of the crystal lattice (phonons), and electronic thermal conductivity (κ_e), which is associated with the movement of charge carriers (electrons and holes) within the material.

$$k_{\text{tot}} = k_l + k_e \quad (9)$$

Thermal conductivity is a key factor in the performance of thermoelectric materials. To achieve high thermoelectric efficiency, materials should have low thermal conductivity while maintaining good electrical properties. Advances in nanostructuring, alloying,

and material design are continually improving the thermal management of thermoelectric materials.



The Wiedemann-Franz law predicts a high correlation between electronic thermal conductivity and electrical conductivity. This law states that the ratio of the electronic contribution to the κ_e to the σ is proportional to the temperature:

$$k_e = L \sigma T = n e m L T \quad (10)$$

where L is the Lorenz number, which is approximately constant for metals and degenerate semiconductors.

Chapter 2 Materials Synthesis and Characterization

2.1 Synthesis Equipment

2.1.1 Spark Plasma Sintering

Spark Plasma Sintering (SPS) is one of the various methods for sintering materials.

It operates by applying a direct current voltage to a mold, causing the material to enter a plasma state. To achieve good electrical conductivity, the molds are made of graphite.

High pressure is then used to compress the powdered material tightly within the mold.

By adjusting the current, the temperature can be controlled and maintained at the target value. The key advantage of this method is its rapid heating and cooling, resulting in a very short overall processing time that can be completed in a few minutes.

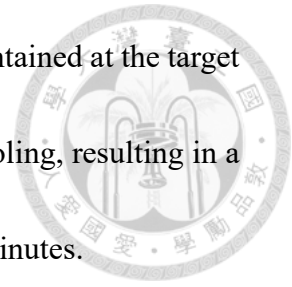


Fig.I.1. 5 Spark plasma sintering (SPS).

2.1.2 RF Magnetron Sputtering

Sputtering is a physical vapor deposition (PVD) process used to process the thin films on a substrate. The working principle of RF magnetron sputtering is using an

alternating radio frequency is used to ionize the sputtering gas (typically argon), generating plasma. The ions generated in the plasma bombard onto target material, causing atoms to be ejected. The ejected atoms then move through the vacuum chamber and settle onto the substrate, creating a thin film.

In this experiment, BST films were prepared by using the RF magnetron sputtering technique, a specific type of sputtering technique that employs radio frequency (RF) to generate plasma and sputter material from the target onto the substrate.



Fig.I.1. 6 2-inch RF magnetron sputtering system

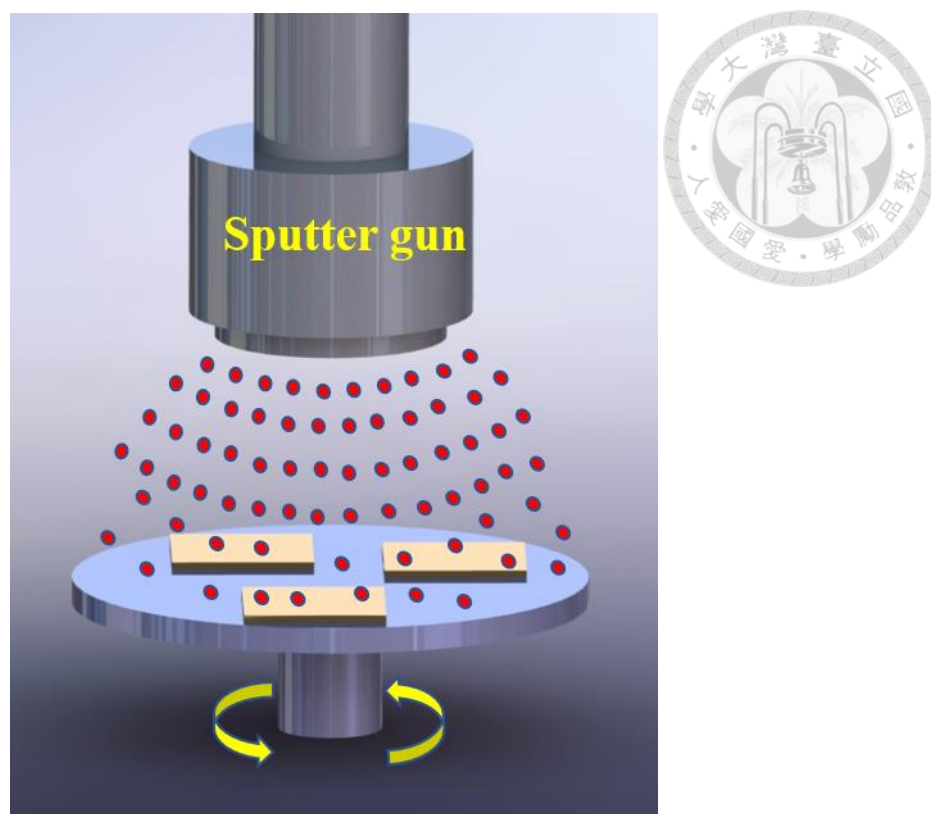


Fig.I.1. 7 Sputtering schematic.

2.2 Experimental Equipment

2.2.1 X-ray Diffraction

XRD is a strong analytical method for detecting and characterizing a material's crystallographic arrangement, chemical composition, and physical characteristics of a material. X-ray diffraction (XRD) is a basic X-ray diffraction technique that measures the angles and intensities of X-rays scattered by atoms within a material. In our investigation we utilized XRD, PANalytical X'Pert Pro fitted with Cu $K\alpha$ radiation (0.154 nm) to ascertain the crystal orientation of the films. Textural elements in the thin layer suggest a preferred orientation within the structure. Pole figures, which can be

generated using a threefold diffractometer (Malvern Panalytical's Materials Research Diffractometers, MRD), are commonly used to define this preferred orientation.



Fig.I.2. 1 X'pert Pro Panalytical x-ray powder diffractometer and four-circle diffractometer.

2.2.2 Scanning Electron Microscope

Scanning Electron Microscopy (SEM) one of the powerful instrument used to analyze surface morphology and microstructural features of a materials by scanning a focused beam of electrons on the sample's surface. The interactions between the electrons and the atoms in the sample generate various signals that produce high-resolution images.

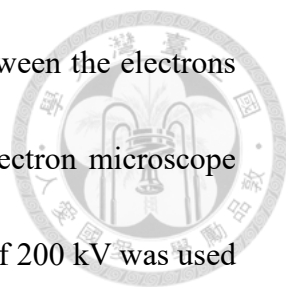
Field emission scanning electron microscopy was used to examine the microstructures of the films. With the use of energy-dispersive X-ray spectroscopy (EDAX) connected to the SEM, thin films' composition was ascertained. This combination of methods enables a thorough analysis of the elemental composition and surface morphology of the films, offering vital insights into the microstructural properties of the material.



Fig.I.2. 2 FESEM, Inspect F FEI

2.2.3 Transmission Electron Microscope

Transmission Electron Microscopy (TEM) is a powerful analytical technique used to study the microstructure of materials at very high spatial resolutions, down to the atomic level. A stream of electrons is passed through an incredibly thin specimen using



a transmission electron microscope (TEM), and the interaction between the electrons and the sample creates a picture. A field emission transmission electron microscope (JEOL JEM-2100, Tokyo, JP) operating at an accelerating voltage of 200 kV was used in our investigation to examine the transmission electron micrographs and selected area electron diffraction (SAED) patterns of the films. Prior to TEM observations, the focused ion beam (FEI Versa 3D, Hillsboro, Oregon, USA) was employed to generate the TEM specimen of the cross-sectional thin film. This process allowed for a detailed examination of the films at the nanoscale, providing valuable insights into their internal structure and crystallographic features.

2.3 Measurement Equipment and Techniques

In the process of researching and developing thermoelectric materials, precise measurement techniques are crucial. The following introduces several commonly used measurement techniques

2.3.1 LFA

The LFA (Laser Flash Analyzer) is a precision instrument designed to measure the thermal diffusivity of materials. Manufactured by NETZSCH, the LFA is extensively used in research and industrial purposes to characterize the thermal properties of

various materials, including metals, ceramics, polymers, and composites. The LFA measures thermal diffusivity (D) using the laser flash method, where a short laser pulse is applied to one side of the sample, and the resulting temperature rise on the opposite side is recorded. The time it takes for the heat to traverse the sample is used to calculate the thermal diffusivity. Using the formula $\kappa = D\rho C_p$, where κ is the thermal conductivity, ρ is the density was measured by Archimedes method, and C_p is the specific heat by using all these parameters one can determine the thermal conductivity.



Fig.I.3. 1 LFA 447

2.3.2 TDTR

Time-Domain Thermoreflectance (TDTR) is an advanced measurement technique used to analyze the thermal properties of materials, such as thermal conductivity, thermal diffusivity, and interfacial thermal resistance. TDTR [10] employs ultrafast laser technology to observe the temperature changes in materials following interaction with a laser pulse, enabling the analysis of the material's thermal characteristics.

2.3.3 ZEM-3

The ZEM-3 [11] is a high-precision instrument designed to measure the Seebeck coefficient and electrical conductivity of thermoelectric materials. It is widely used in research and development settings to evaluate the performance of these materials. When measuring the Seebeck coefficient of a sample, the heater provides a current to create a temperature difference between the top and bottom ends of the sample. Temperature sensors measure the temperature difference (ΔT) at the points where the sensors contact the sample. The circuit can also be switched to measure the voltage difference (ΔV) induced by the Seebeck effect at these contact points using the wires inside the temperature sensors. The Seebeck coefficient at the ambient temperature is

then determined using the definition of the Seebeck coefficient.

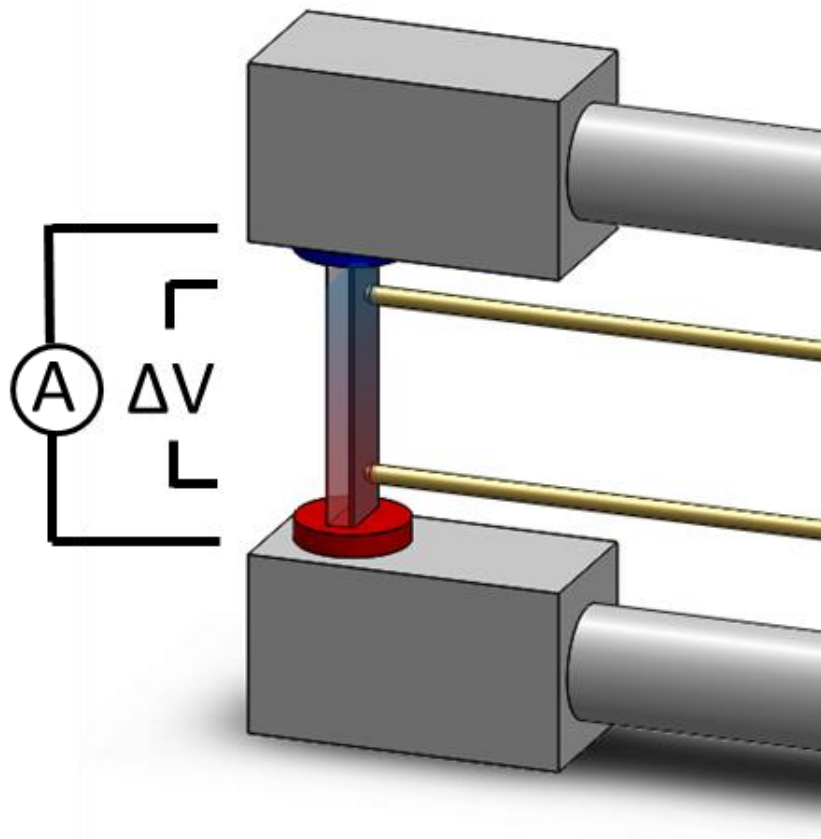
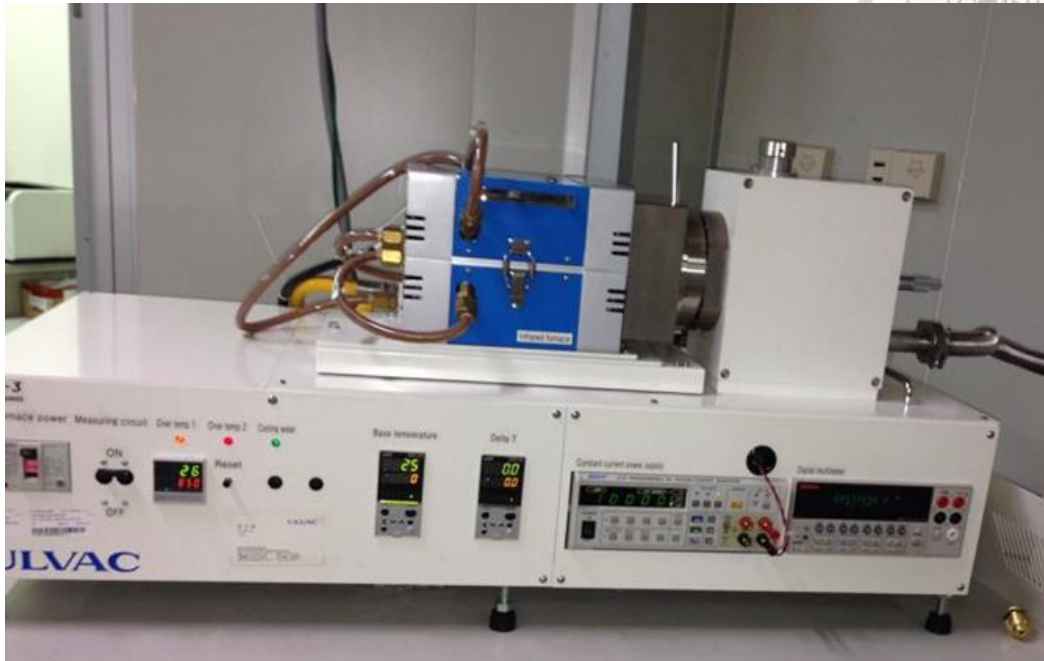


Fig.I.2. 3 ZEM-3 instrument and schematic

2.3.4 PPMS

Hall Effect Measurement with PPMS involves preparing a sample with a well-defined geometry, typically a thin rectangular strip, where electrical contacts are made at the corners for current injection and voltage measurement. The sample is then mounted on a sample holder and placed in the PPMS chamber. The sample holder connects to the PPMS power supply and meter, allowing for precise control of the current, voltage measurement, and application of a magnetic field during the experiment.

The Hall voltage is used to calculate the Hall coefficient (R_H) [12], which is related to the carrier concentration (n) by the equation:

$$R_H = \frac{E_y}{J_x B_z} = \frac{V_H t}{IB} \quad (11)$$

where E_y is the Hall electric field, J_x is the current density, B_z is the magnetic field, V_H is the Hall voltage, t is the sample thickness, and I is the current. From the Hall coefficient, the carrier concentration can be determined using the equation $n = 1/eR_H$, where e is the elementary charge. The mobility (μ) is calculated using the resistivity (ρ) and Hall coefficient $\mu = R_H/\rho$.



Fig.I.3. 2 PPMS

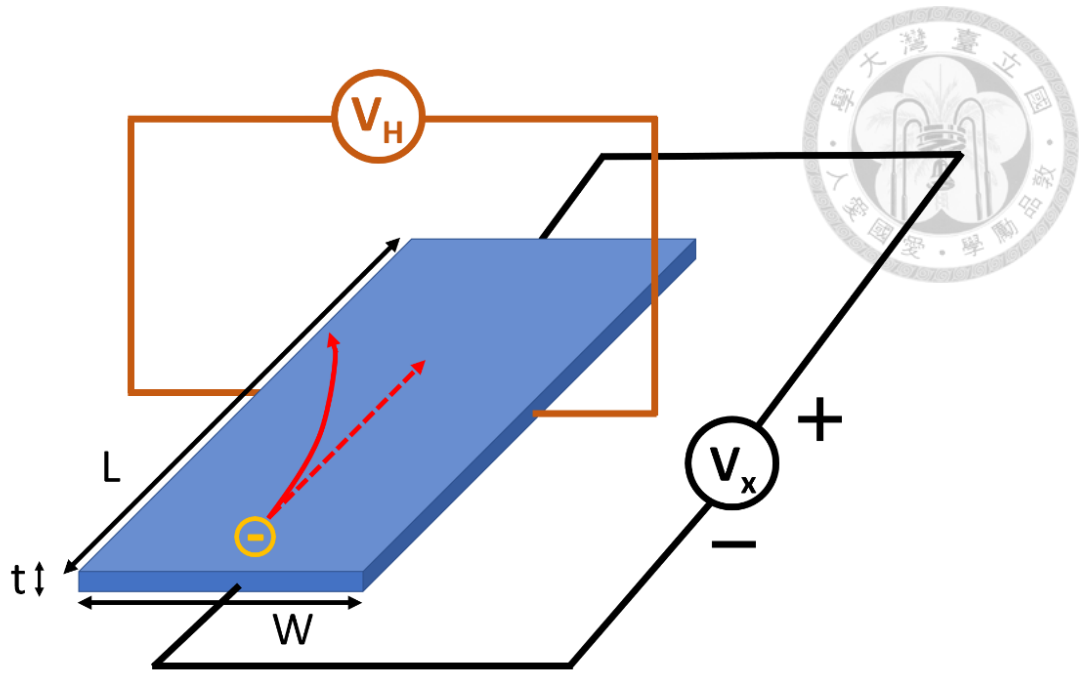


Fig.I.2. 4 Hall measurement

2.3.5 3ω technique

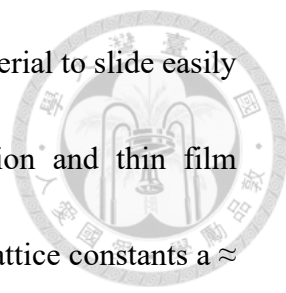
The 3ω technique, commonly used to measure a material's thermal conductivity, was employed in a high vacuum (1×10^{-6} torr) to minimize heat losses from air. We used a lock-in amplifier and a AC and DC current source (Keithley 6221). With this configuration, it was possible to perform extensive tests typically linked with a dual-phase lock-in amplifier. These measurements include input signal's noise level, vector magnitude, phase angle, and in-phase and quadrature components.

Chapter 3 Introduction of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ Materials

$\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ is a compound composed of bismuth (Bi), antimony (Sb), and tellurium (Te), and it is most widely researched and utilized materials for thermoelectric applications. $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ was particularly notable for its high thermoelectric performance at room temperature, making it an excellent candidate for various energy conversion applications. Devices utilizing this material can directly generate electricity from temperature differences or produce cooling effects using electricity. It is used to make thermoelectric generators that transform waste heat into electricity and is widely applied in industrial equipment, automobiles, and wearable devices.

3.1 Composition and Structure

$\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ belongs to the class of bismuth tellurides, which are known for their layered crystal structures. Typically, it consists of quintuple layers, was stacked along the c-axis. The layered structure is composed of bismuth, antimony, and tellurium atoms, arranged in a sequence of five atomic layers: two layers of Te atoms, one layer of Bi atoms, one layer of Sb atoms, and another layer of Te atoms. This layered arrangement gives the material strong anisotropy in the direction perpendicular to the layers. In $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$, the atoms within the layers are primarily bonded by covalent and partially ionic bonds, while the layers themselves are held together by van der Waals bonding.



Consequently, the interlayer interactions are weak, allowing the material to slide easily between layers, which is advantageous for mechanical exfoliation and thin film preparation. $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ has a hexagonal crystal phase where the lattice constants $a \approx 4.26 \text{ \AA}$ and $c \approx 30.4 \text{ \AA}$. This crystal structure helps suppress thermal conductivity because the arrangement and vibrational modes of atoms in the layered structure can efficiently scatter phonons, thereby reducing thermal conductivity and enhancing the thermoelectric figure of merit (ZT). Due to the mixture of Bi and Sb, $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ has a complex electronic structure, which gives it a high Seebeck coefficient and electrical conductivity at room temperature. The conduction and valence bands near the Fermi level have a high density of states, which is advantageous for the thermoelectric transport of charge carriers. The layered structure, bonding characteristics, crystal structure, and electronic structure of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ collectively determine its excellent thermoelectric performance [13-16], making it highly promising for various thermoelectric applications.

Chapter 4 Materials Synthesis and Characterization



4.1 Material Synthesis

This chapter introduces the equipment used for characterizing the samples.

4.1.1 The Bulk $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ Sputtering Target's Preparation

With a 99.999% purity level, the elements Bi, Sb, and Te were weighed in a 0.5:1.5:3 stoichiometric ratio. These elements were kept into a quartz tubes, evacuated, and then heated to 1023 K for 24 hours. The tube was then rapidly quenched into a cold water. The resultant ingots samples were subjected to a 48-hour annealing procedure at 723 K. The ingots were crushed into powders using an agate mortar after annealing.

These powders were compacted using the spark plasma sintering (SPS) method under vacuum at 673 K and a pressure of 50 MPa for 5 minutes, forming a dense pellet with a diameter of 50.8 mm and a height of 20 mm. This pellet was subsequently used as a target in the sputtering process.

4.1.2 Film Deposition and Annealing of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ (BST)

The technique known as RF magnetron sputtering was employed to create BST films. The experiment was conducted using Corning 1737F glass substrates, which had

a surface roughness ranging from 0.5 to 1.0 nm and measured $20 \times 20 \text{ mm}^2$. In an ultrasonic bath, the substrates were extensively cleaned many times using acetone, isopropyl alcohol, and deionized water in that order. 45 mm was the constant distance between the substrates and the target. While the working pressure of the sputtering gas was controlled at 7×10^{-3} torr with an argon flow rate of 20 sccm, the base pressure of the deposition chamber was maintained below 7×10^{-7} torr. With the sputtering power adjusted to 30 W, a deposition rate of about 20 nm per minute was achieved.

It has been shown that post-deposition annealing in a Te environment can provide virtually perfect stoichiometry for the film composition of V-VI semiconductors. Tellurium powder was placed within an evacuated quartz ampoule, which was post-annealed after the film was deposited at 453 K. For three days, the post-annealing procedure was carried out at 473 K.

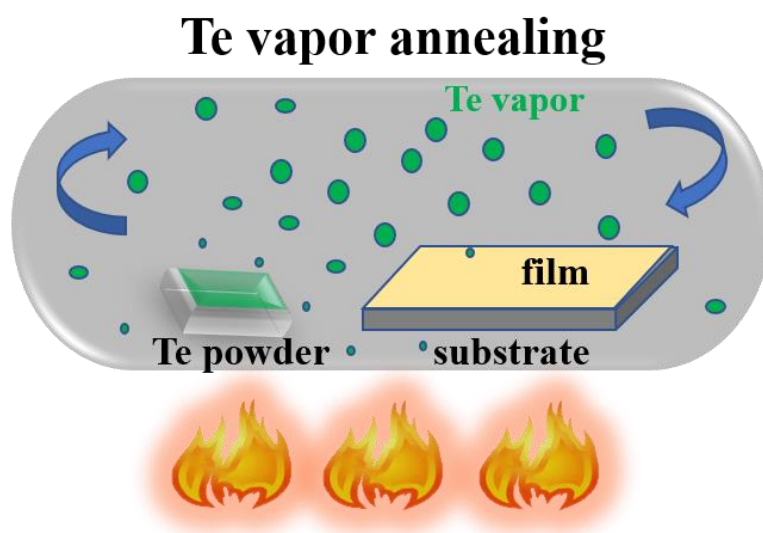


Fig.I.4. 1 Te vapor annealing schematic

Firstly, regarding the Seebeck coefficient, it is approximately in the range of 146 to 170 ($\mu\text{V/K}$). After Te annealing [17,18,19,20], the values significantly increase to approximately 195 to 205 ($\mu\text{V/K}$). To attain a high ZT value, a higher Seebeck coefficient is necessary, so the purpose of Te annealing is achieved. Figure 4-12 is a comparison of the Seebeck coefficient for the thermoelectric thin films with different thicknesses before and after annealing.

In terms of resistivity, the resistivity of films with various thicknesses is all above 60 ($\mu\Omega\text{-m}$) before Te annealing. To achieve a better ZT value, a lower resistivity is essential. After Te annealing, the resistivity also shows a significant decrease. The resistivity of samples with various thicknesses decreases by about 50%. Figure 4-13 shows the comparison. However, demonstrating the beneficial effect of Te annealing on resistivity.

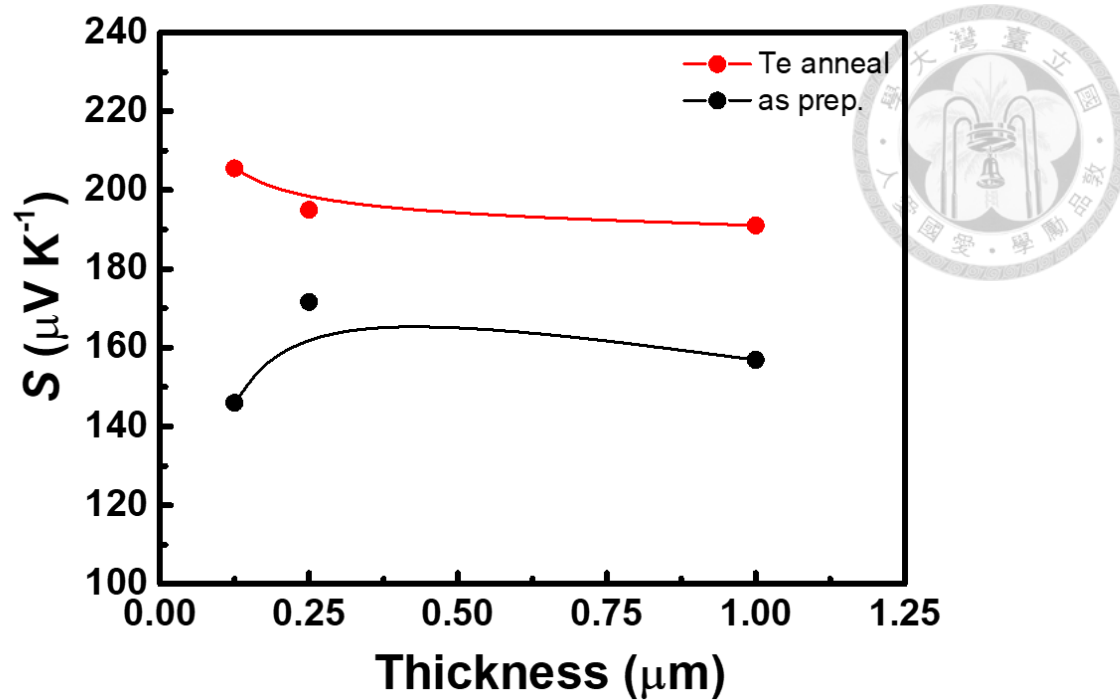


Fig.I.4. 2 Comparison of the Seebeck coefficient before and after annealing

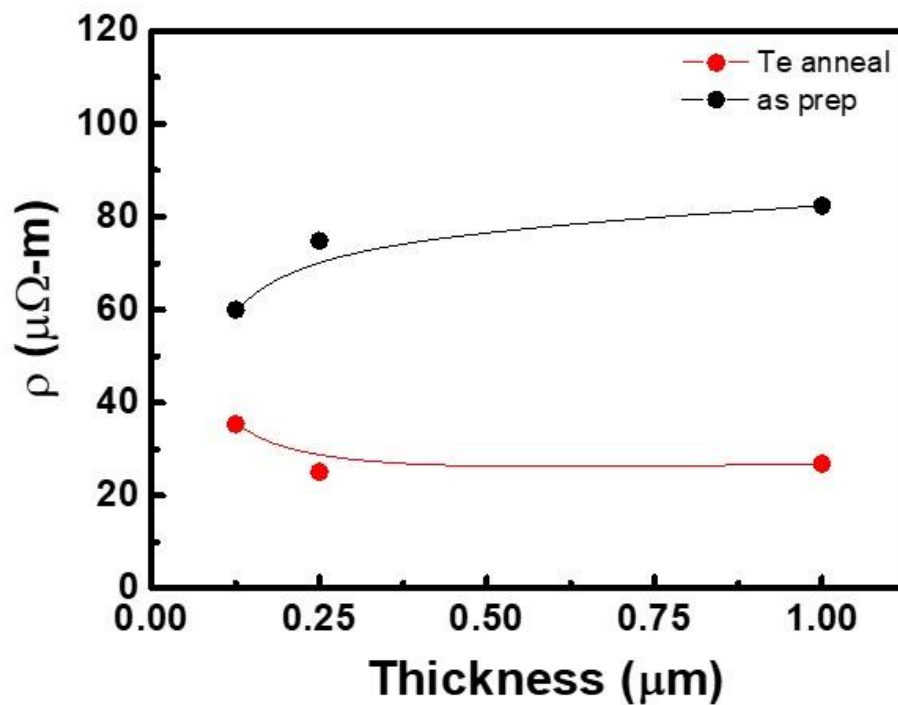


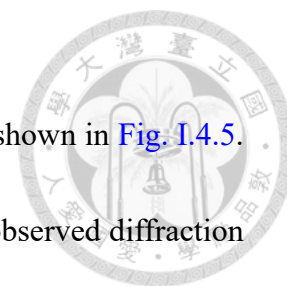
Fig.I.4. 3 Comparison of the resistivity before and after annealing

4.1.3 $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ Film Structural Characterization

The XRD patterns for the deposited films upon annealing are shown in [Fig. I.4.5](#).

The rhombohedral $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ phase is responsible for all of the observed diffraction peaks, and no impurity phases were found to be present within the detection limit. It is interesting to notice that as the thickness increases, the initially preferred orientations (006) and (10 10), which were more prevalent in thinner films, gradually decrease. Only at (015) is a noticeable peak visible for films thicker than 1 μm ; other peaks seem extremely weak and are obscured. This suggests that the preferred orientation in the (015) direction increases with increasing film thickness.

SEM pictures of BST films with different thicknesses, including surface and cross-sectional views, are shown in [Fig. I.4.4 b-e](#). The grain sizes of the films range from 20 to 50 nm, and their surfaces are flat. Notably, a stacked layer with no discernible growth direction is shown close to the substrate in the cross-sectional morphology of the 1 μm thick film. Following this, the grains mostly develop in the direction in which they are most inclined to grow, creating distinctive microcrystalline formations that resemble slanted sheets. The hypothesized Stranski-Krastanov film growth model is supported by these images, which align with the structural evolution patterns found in the XRD data.



BST adatoms progressively cover the substrate surface during the first phase of film development, generating nuclei. The adatoms acquire enough energy to diffuse across the substrate surface until it is completely covered when the substrate temperature hits 453 K. As the nuclei enlarge, they often take on a plate-like shape with an orientation of (00L). New adatoms keep coming in to fill the spaces between these plates in the meantime. As the film deposition advances, preferential growth along the (015) and (1010) orientations is caused by the sputtering deposition process's low substrate temperature, high nucleation rate, and slower crystal growth rate. Films with (015) and (1010) orientations still display a tightly packed structure, as seen in Fig. I.4.4 d and f, and this does not negatively impact the conductive pathways. The films' predominant elemental composition of Bi, Sb, and Te in a ratio of 0.5:1.5:3, or $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$, is confirmed by EDX analysis.

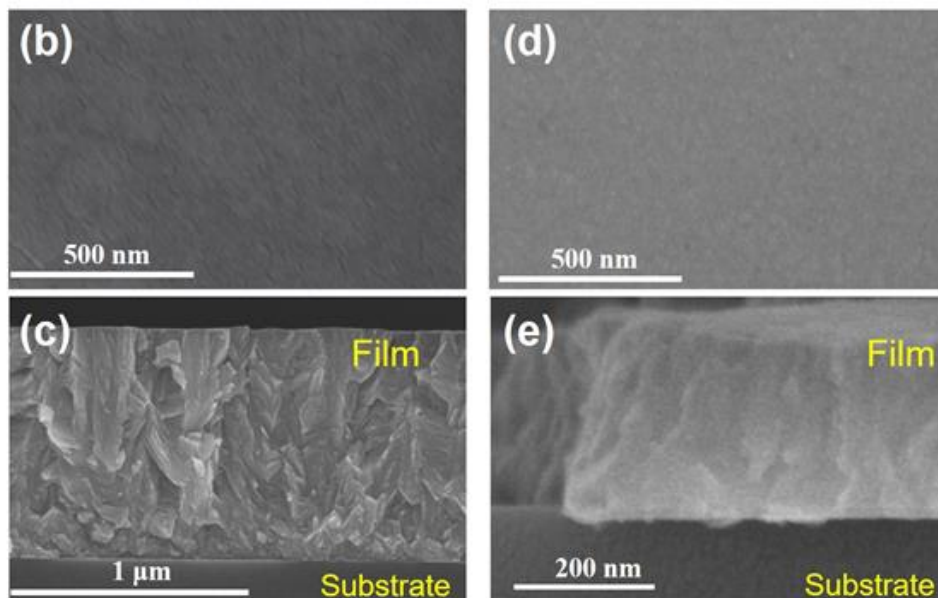


Fig.I.4. 4 Films SEM images

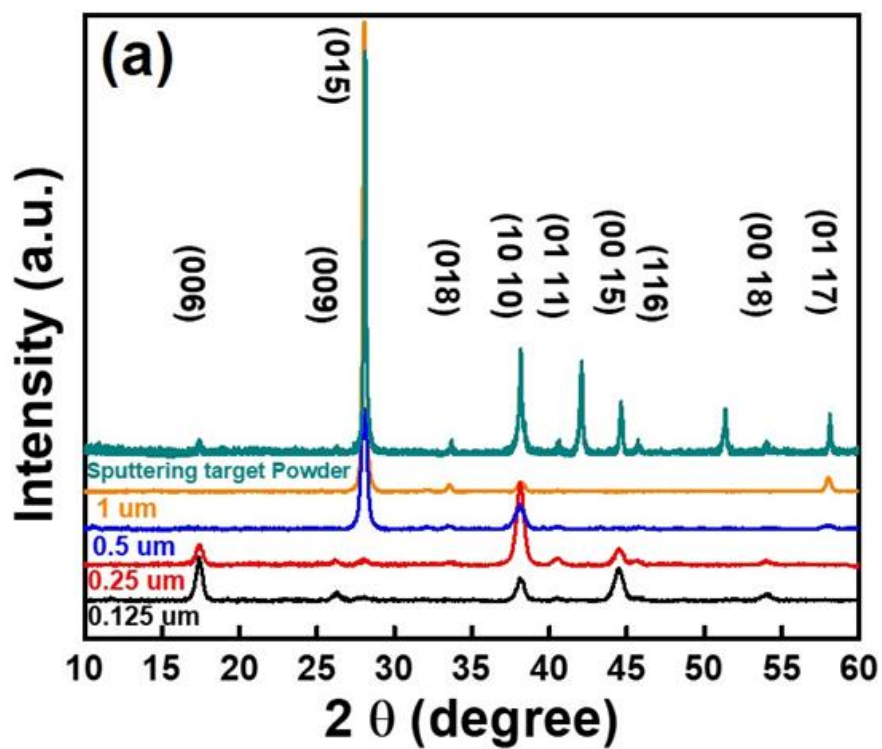


Fig.I.4. 5 Films XRD results

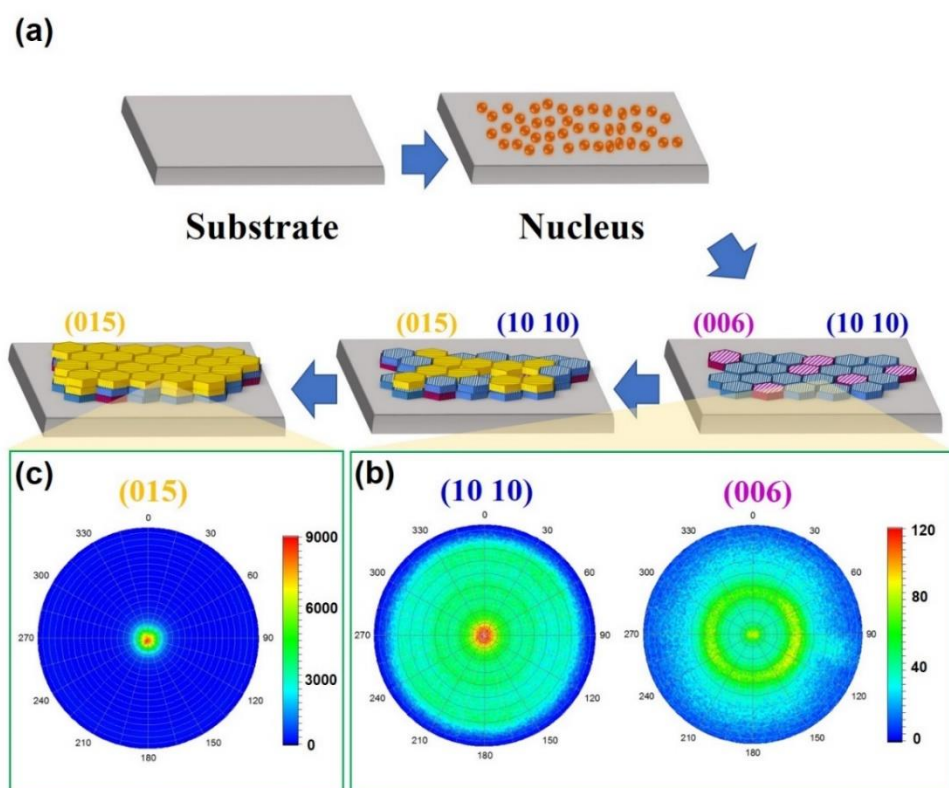


Fig.I.4. 6 Highly textured $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ thin films fabricated by magnetron sputtering.

This procedure is succinctly illustrated in [Fig I.4.4](#). By rotating the sample along two axes and keeping the diffraction angle equal to the desired Bragg reflection, a pole figure is created that allows one to see the distribution of microcrystalline orientations inside the film. The (006) and (10 10) pole figures show a combination of spot and ring patterns for the thinner 0.25 μm film, suggesting a polycrystalline sample with uniaxial texture ([Fig I.4.6b](#)). On the other hand, the thicker 1 μm film exhibits a highly textured structure with concentrated intensity near the center of the (015) pole image ([Fig I.4.6c](#)).

The (015) and (10 10) planes' tilt angles with regard to the ab plane in the crystal structure of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ are 54° and 33° , respectively. These findings imply that the first phase of film deposition has a comparatively random film orientation and that the process of selective film growth is intimately linked to the formation of texture. In general, the substrate has a significant impact on the crystal orientation of the deposited film. The amorphous glass substrate utilized in this investigation should have minimal effect on the deposited film's crystal orientation. On the other hand, in the early stages of film deposition, some oriented grains might develop more preferentially.

Under the combined effect of thermodynamic and kinetic factors, thin film growth usually proceeds through multiple stages: nucleation, island creation, island merging, development of continuous structures, and thickness growth. The behavior of thin film growth is typically explained using thermodynamic growth models, which consider the

relative surface energy of the substrate (ϵ_s), interface (ϵ_i), and heteroepitaxial layer (ϵ_f).

When defining the growth model, the change in surface energy, $\Delta\epsilon = \epsilon_f + \epsilon_i - \epsilon_s$, is essential since it shows how the substrate wets during film deposition. Incomplete

wetting happens when $\Delta\epsilon > 0$, which causes discontinuous three-dimensional (3D)

islands to grow (Volmer-Weber mode). On the other hand, the deposited material wets

the substrate and grows in a two-dimensional (2D) way layer by layer when $\Delta\epsilon \leq 0$ and

the lattice mismatch is small. The deposited material grows in a two-dimensional (2D)

manner (Frank-van der Merwe mode) by wetting the substrate layer by layer. When

there is a considerable lattice mismatch ($\Delta\epsilon < 0$), growth starts with a wetting layer that

forms a 2D structure. However, as the film thickness develops, ϵ_i is affected by thermal

stress and strain energy, which eventually leads to the production of 3D islands

(Stranski-Krastanov mode). The growth behavior of sputter-deposited BST films is

consistent with the Stranski-Krastanov model, according to XRD analysis and pole

figures. Furthermore, these films exhibit some preference orientations, such (10 10) and

(015), are shown in these movies. These orientations correspond to the lowest surface

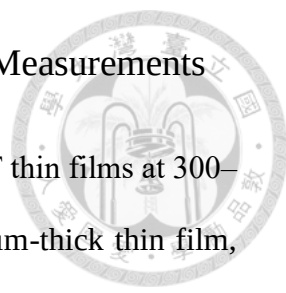
energy planes, which are less damaged by ions during deposition. Preferred orientations

are important because they improve the film's thermoelectric qualities. Certain crystal

configurations also improve the film's electrical and thermal transport qualities, which

further enhances the film's suitability for thermoelectric applications.

4.1.4 Electrical Conductivity and Seebeck Coefficient Measurements



The observed conductivity values (σ) of bulk material and BST thin films at 300–400 K are shown in [Fig. I.4.7a](#). With the exception of the 0.125 μm -thick thin film, which exhibits a progressive increase in conductivity, the bulk material and the other thin film samples exhibit a monotonic decrease in conductivity that is consistent with rising temperatures. The reason for this trend is that BST exhibits conductivity characteristics similar to metallic materials since it is a semiconductor with relatively tiny band gaps. The lowest conductivity is seen in the thinnest sample (0.125 μm), which is probably because there are a lot of contacts in the first phases of the film's formation. Particle size increases and grain boundaries shrink as layer thickness rises, improving conductivity. The sample with the highest conductivity is the one that is 0.5 μm thick. Nevertheless, the conductivity drastically decreases when the film thickness rises to 1 μm . The findings of the Hall measurement show that a decrease in carrier mobility within the film is the main cause of this conductivity fall. Thinner films primarily have (00L) and (10 10) crystallographic orientations, according to XRD studies, which facilitates carrier transport along the ab plane without bridging van der Waals gaps. The predominant preferred orientation shifts to (015) at a film thickness of around 1 μm , in spite of the textured structure. This suggests that carriers meet van der Waals gaps during in-plane propagation, which lowers carrier mobility.

All thin film samples show P-type conductivity according to Seebeck coefficient measurements, and the fluctuation in the Seebeck coefficient closely correlates to the carrier concentration of the films. The thinner 0.125 μm film exhibits the lowest carrier concentration, roughly $3 \times 10^{19} \text{ cm}^{-3}$, even under the same processing conditions. As illustrated in [Fig.I.4.8.](#), the carrier concentration progressively rises with increasing film thickness, leading to a modest drop in the Seebeck coefficient.4.8. Because BST

is a narrow band gap semiconductor, it exhibits a strong bipolar effect at higher temperatures, which may result in a decrease in the Seebeck coefficient in the higher temperature range. Plotted in Fig.I.4.9. is the relationship between S and n_H (Pisarenko relation) at 300 K based on the single parabolic band (SPB) model under the phonon scattering assumption [21]. For an effective mass of $m^* = 1.5 m_e$, the predicted curve and the experimental data agree well. This investigation indicates that the BST alloy's band structure close to the Fermi surface is mostly unaffected by the thin film thickness.

The temperature-dependent change of PF , is shown in Fig. I.4.10. PF , is significantly improved over the whole tested temperature range due to the notable increase in conductivity for the 0.25 μm and 0.5 μm samples. Achieving a high PF , of roughly $18.1 \mu\text{W cm}^{-1} \text{K}^{-2}$ at 400 K, the 0.25 μm sample is on par with samples generated using the pulsed laser deposition approach, albeit being lower than that of bulk material. Furthermore, at 400 K, the PF almost stays the same even though the Seebeck coefficient of the 0.5 μm thin film is somewhat lower than that of the 0.25 μm thin film.

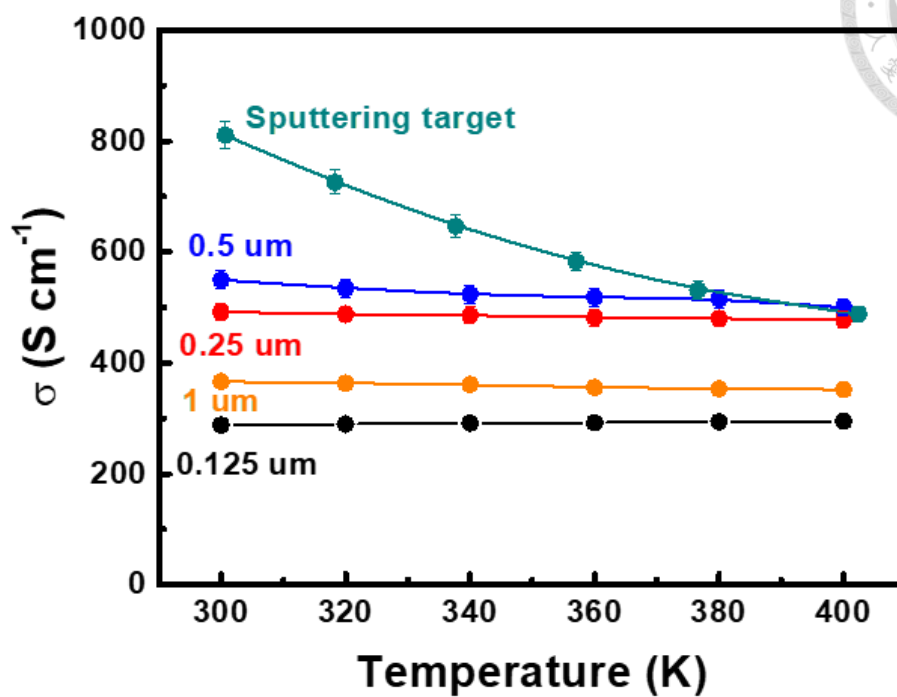


Fig.I.4. 7 Temperature-dependent electrical conductivity.

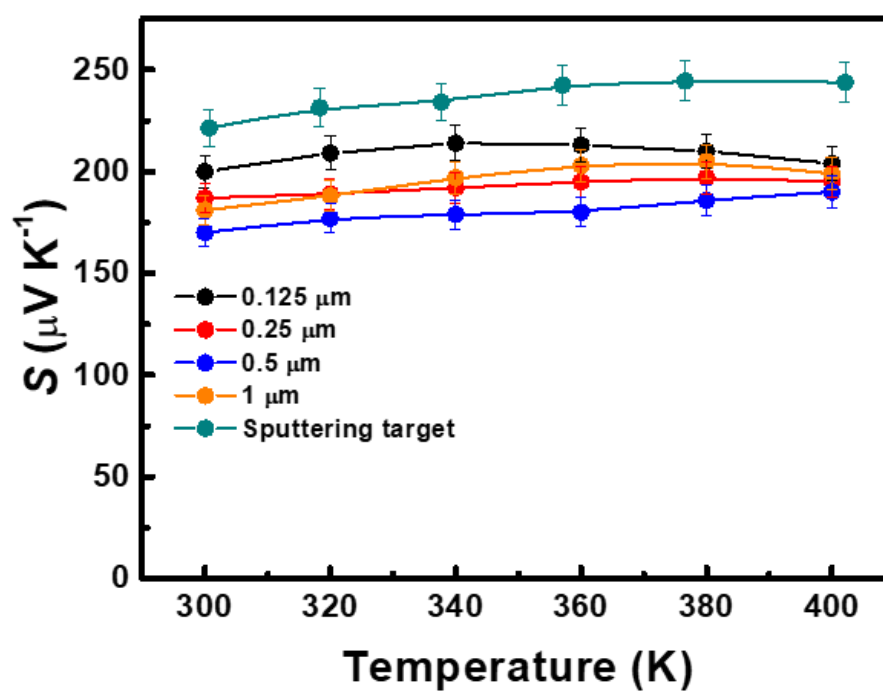


Fig.I.4. 8 Temperature-dependent seebeck coefficient.

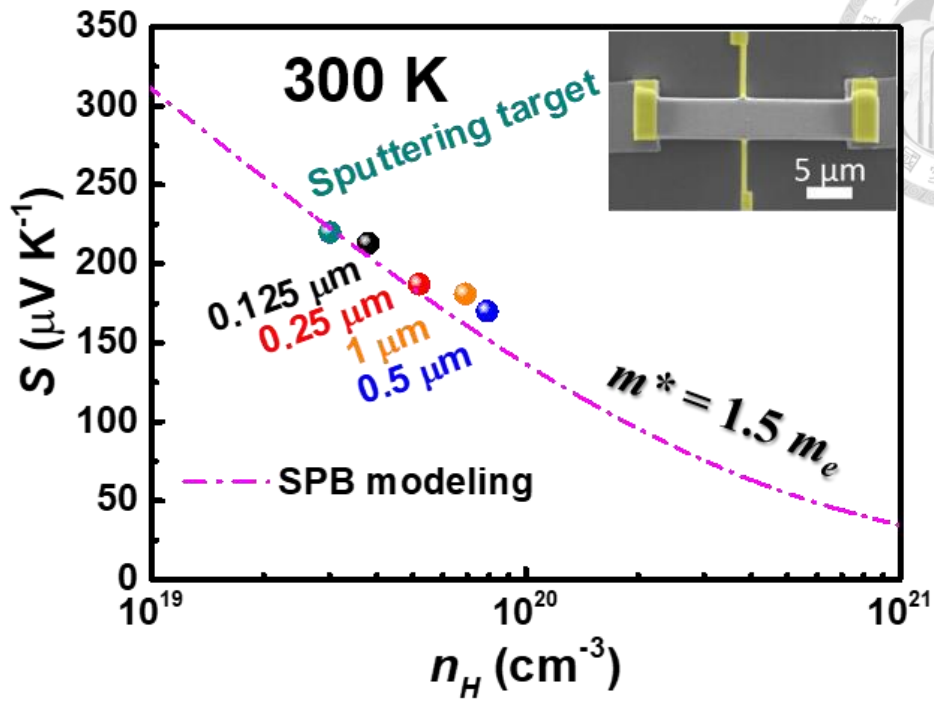


Fig.I.4. 9 Pisarenko relationship at room temperature with effective mass, $m^* = 1.5 m_e$.

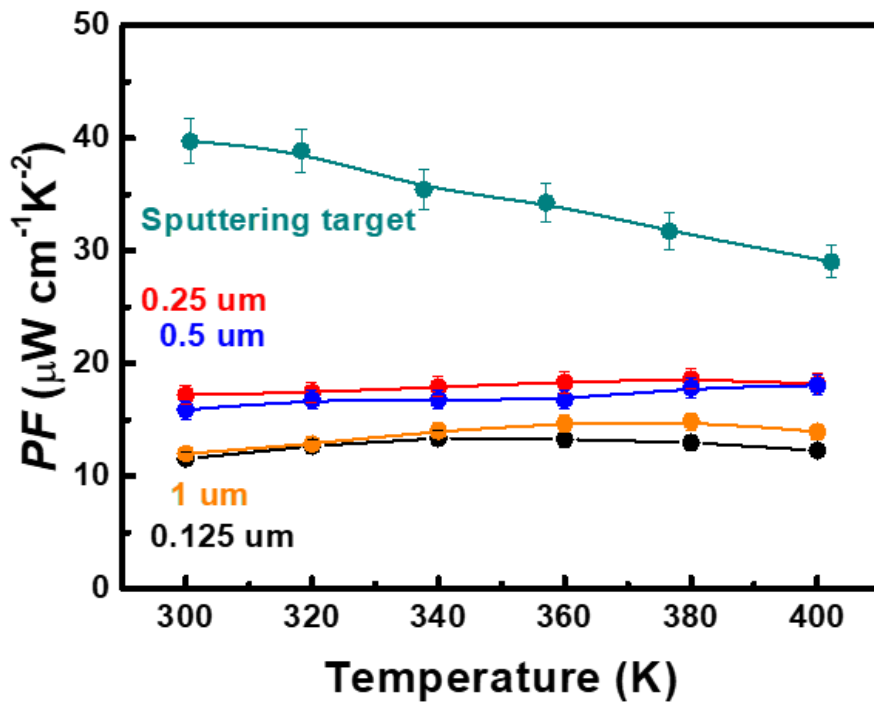


Fig.I.4. 10 Temperature-dependent power factor.



4.1.5 Thermal Conductivity Measurements of Film

Thin-film thermal conductivity measurements are challenging. In this work, we measured the in-plane thermal conductivity using the well-established 3ω method in our lab. Suspending the test sample is an essential step before measurement to precisely determine the true K of the thin film. We developed a novel strategy to achieve this, as shown in [Fig. I.4.11](#). Using a scalpel, thin films of approximately $100 \times 100 \mu\text{m}^2$ are first carefully removed from the substrate. Currently, the minimum practical thickness for extremely thin films is approximately $0.5 \mu\text{m}$. The detachable thin film is then sliced precisely with a Focused Ion Beam (FIB) to form a rectangular shape that has a ratio of length to cross-section similar to a belt or rod. The observance of the boundary conditions necessary for the 3ω measurement is guaranteed by this particular ratio [\[21,22,23\]](#). The resultant extended sample is carefully put onto a measuring chip with pre-fabricated electrodes after being handled with a probe and suspended using van der Waals forces. After the sample is firmly in place, the piece of the sample that comes into contact with the electrodes is welded using the FIB once more, allowing for the subsequent 3ω thermal conductivity measurements [\[24-26\]](#).

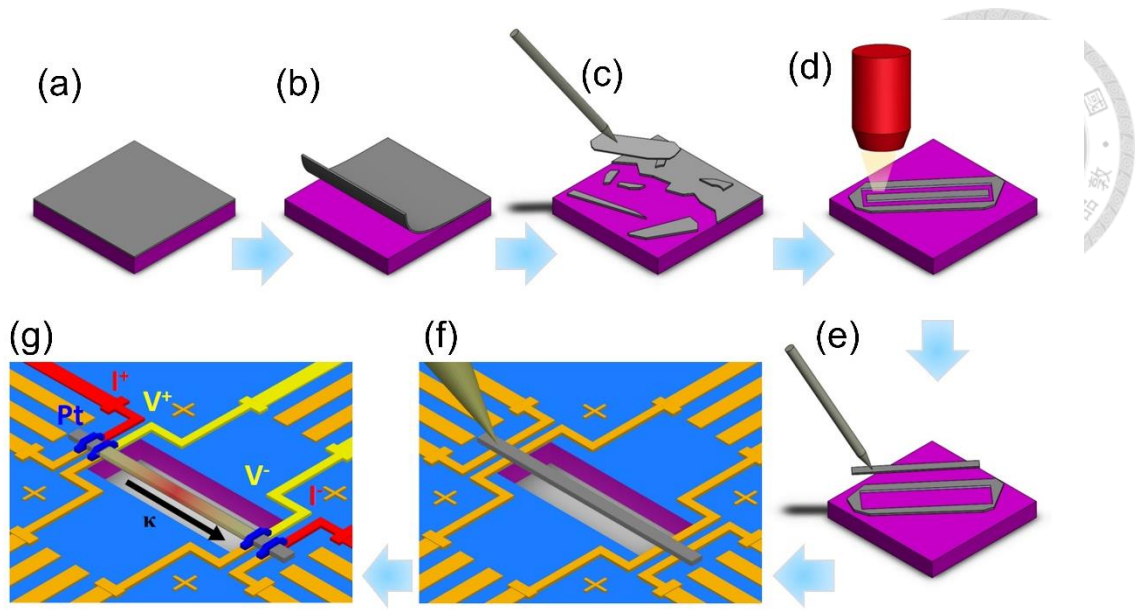


Fig.I.4. 11 (a)-(g) show the sample preparation procedure for in-plane thermal conductivity measurements of films.

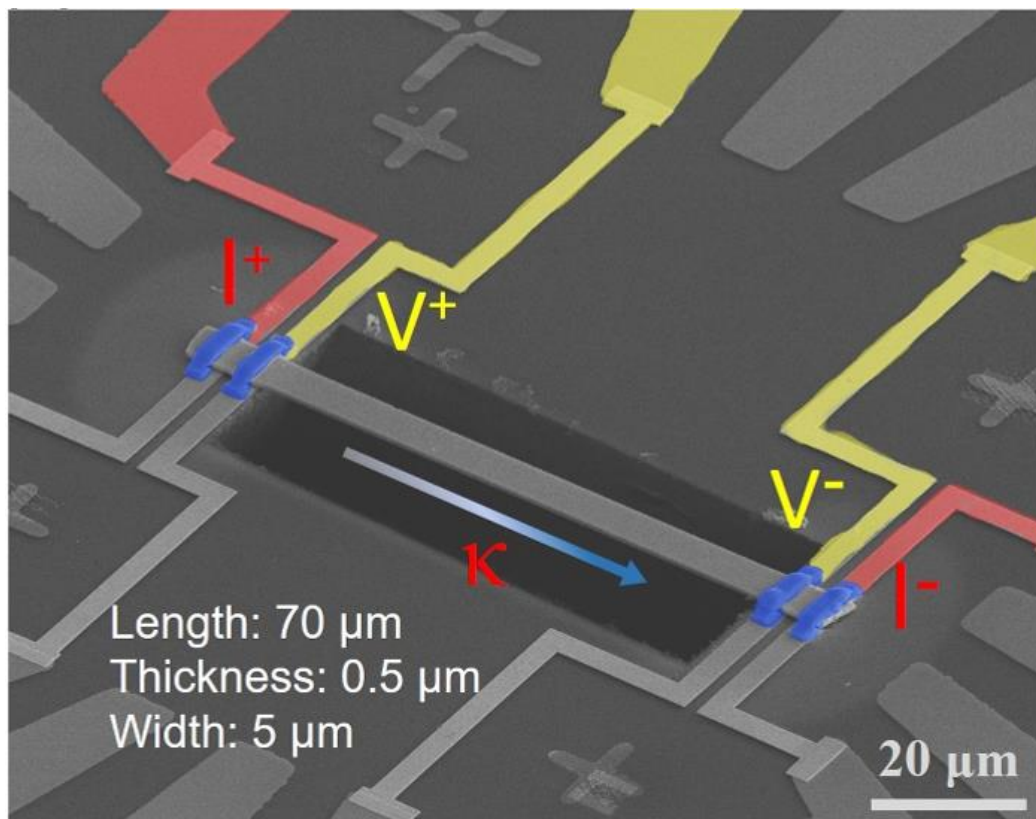
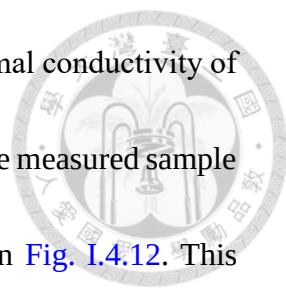
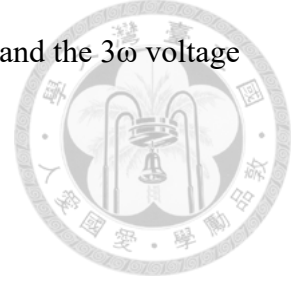


Fig.I.4. 12 SEM image of a sample suspended for measurements.



The 3ω method is a reliable technique for determining the thermal conductivity of one-dimensional materials. The actual suspended configuration of the measured sample and the functions of the different contact electrodes are depicted in [Fig. I.4.12](#). This method requires the sample to be a conductor with temperature-dependent resistance. The sample functions as both a thermometer and a heater. When the sample is exposed to an AC current ($I_0 \sin \omega t$), there is a 2ω temperature change (also known as temperature fluctuation) and a corresponding 2ω resistance variation (also known as resistance fluctuation). As shown by the mathematical calculations and the schematic in [Fig. I.4.13](#), this results in a voltage fluctuation at the 3ω frequency. The voltage signal is measured at the center of the sample, and AC current is supplied from both ends during the measurement process. The sample is suspended on a hollowed-out chip to prevent heat loss through the substrate. This setup enables the simultaneous measurement of the one-dimensional material's specific heat, electrical resistivity, and thermal conductivity. A noticeable temperature difference is generated between the sample's ends due to Joule heating instigated by the current flowing through it. A high vacuum environment is required to prevent heat loss by radiation or convection. Furthermore, the heat generated by the sample and its diffusion can be described by a differential equation with appropriate boundary conditions. The cited literature provides a thorough derivation and explanation of the formula. Equation (12) expresses

the mathematical relationship between the thermal conductivity (κ) and the 3ω voltage ($V_{3\omega}$) signal [27,28,29,30,31].



$$V_{3\omega} \approx \frac{4I^3 L R R'}{\pi^4 \kappa A \sqrt{1 + (2\omega\gamma)^2}} \quad (12)$$

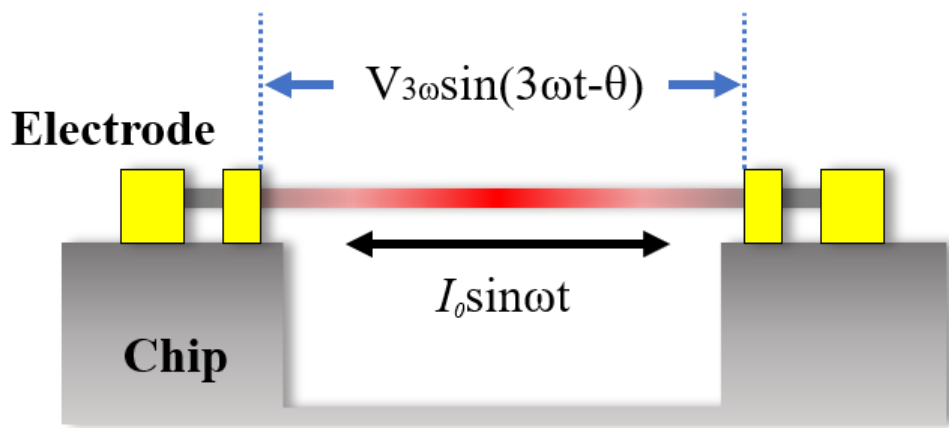


Fig.I.4. 13 3ω method schematic.

In this equation, κ stands for thermal conductivity, A for the sample's cross-sectional area, ω for the AC current frequency passing through the sample, L for the sample's length, R for resistance, R' for the rate at which resistance changes with temperature, and γ for the sample's characteristic thermal time constant. Every data point shown in [Figure I.4.14](#) is the result of fitting the frequency dependence of $V_{3\omega}$ to equation (13).

$$V_{3\omega} \propto 1/\sqrt{1 + (2\omega\gamma)^2} \quad (13)$$

The fitting outcome at 300 K for the 0.5 μm film is shown. Equation (14) illustrates how the intercept of the fitted line at this temperature can be used to calculate the thermal conductivity κ .

$$V_{3\omega} \approx \frac{4I^3 LRR'}{\pi^4 \kappa A} (\omega\gamma \rightarrow 0) \quad (14)$$

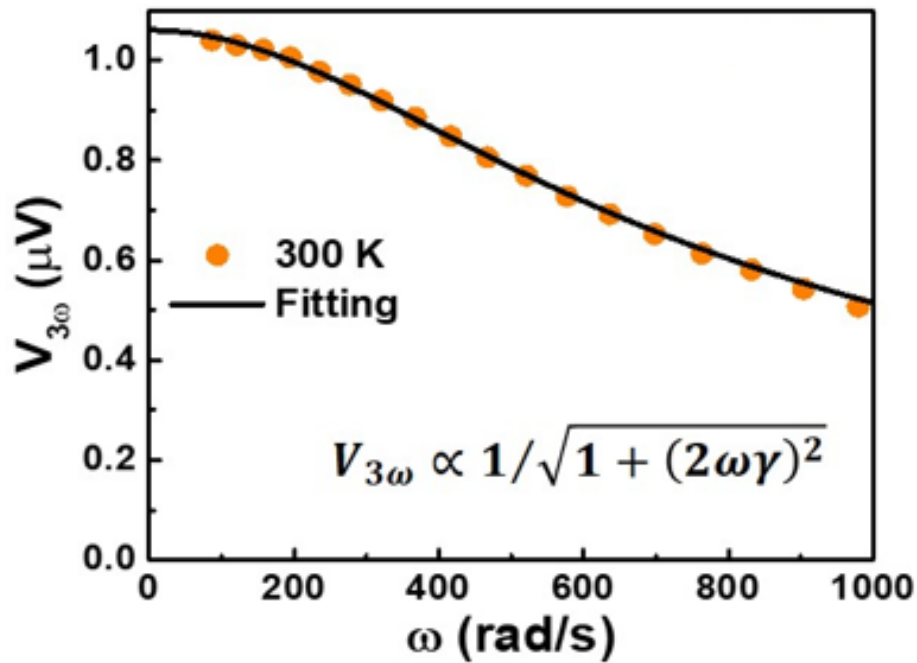


Fig.I.4. 14 Frequency dependence analysis of the angular frequency from the 0.5 μm thick film at 300 K.

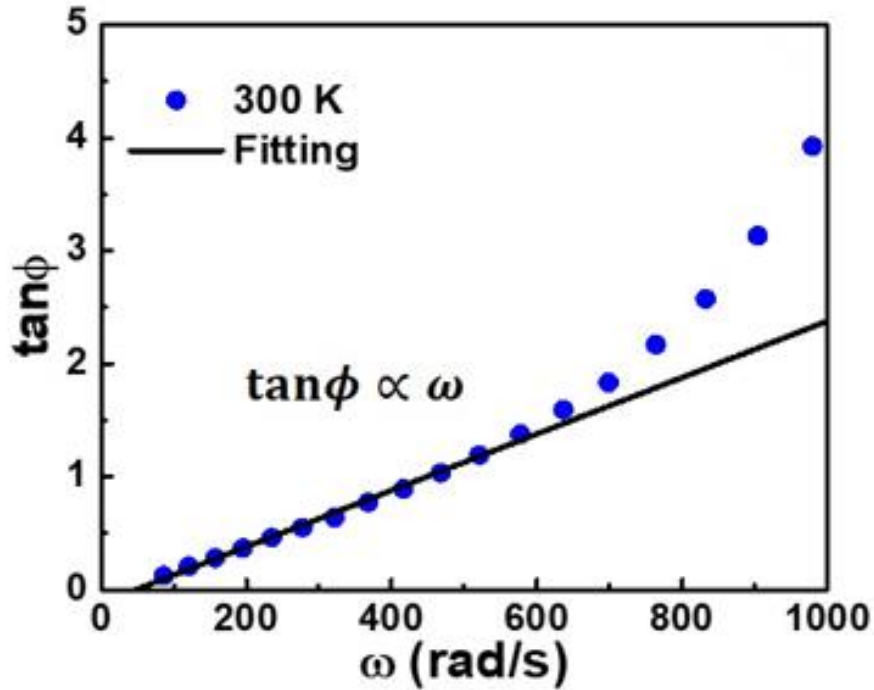


Fig.I.4. 15 Analysis of the $\tan\phi$ dependence on the angular frequency for the 0.5 μm thick film at 300 K.

The phase angle $\tan\phi \approx 2\omega\gamma$ and its relationship to ω are shown in Fig. I.4.15. The appropriate frequency range for frequency-dependent measurements is indicated by $0 < 2\omega\gamma < 4$. Along with the thermal conductivity measurements of BST bulk material in the same direction as the *PF* measurements, Fig. I.4.12 shows the measured thermal conductivity of BST thin films in the temperature range of 300 to 400 K. As illustrated in Fig. I.4.12, the thermal conductivity of the thin films was determined with an uncertainty of less than 5% using the 3ω method. It is noteworthy that, given the extremely low thermal conductivity of the thin films, we first used the

LFA approach to determine the thermal conductivity of the bulk material to confirm the accuracy of the measurement technique. Additionally, we sliced the bulk material into thin specimens with an aspect ratio of about 14 and a thickness of approximately 2 μm by following the sample preparation procedure shown in Fig. I.4.16, using the same sample and ensuring that measurement procedures were followed consistently. This methodical process is necessary to meet the strict standards required for measurements using the 3ω method.

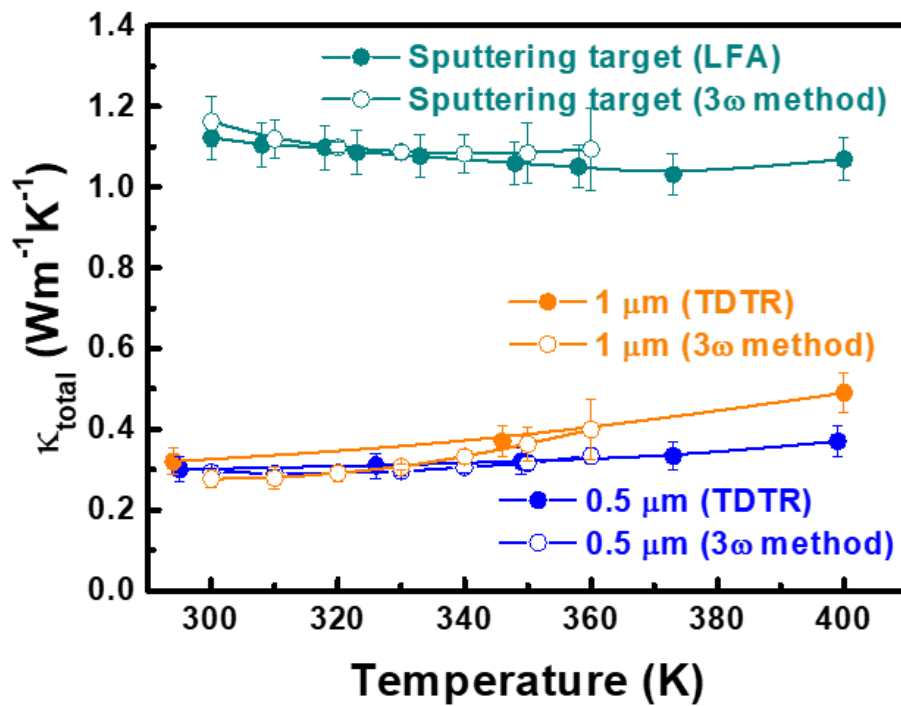
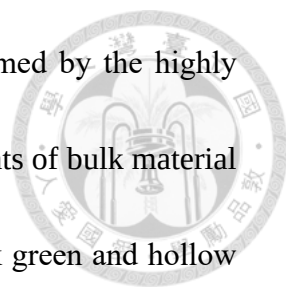
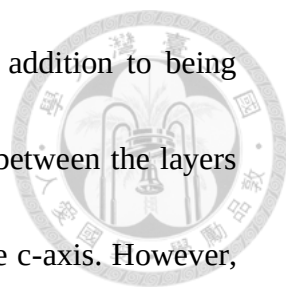


Fig.I.4. 16 The results of the 3ω technique and LFA on the sputtering target are compared with the thermal conductivity measurements for the 0.5 μm and 1 μm films, which were produced using the TDTR method.



The reliability of the 3ω measurement method has been confirmed by the highly consistent findings obtained from thermal conductivity measurements of bulk material using both the LFA and 3ω methods, as indicated by the solid dark green and hollow dark green points in Fig. I.4.16. However, the current practical limit is represented by a thickness of $0.5\ \mu\text{m}$ due to the difficulties in detaching the film from the substrate. Consequently, although the $0.25\ \mu\text{m}$ film sample showed a notable improvement in PF , an accurate in-plane thermal conductivity measurement was not possible. Furthermore, the thermal conductivity values for the 0.5 and $1\ \mu\text{m}$ films were only approximately $0.30\ \text{Wm}^{-1}\text{K}^{-1}$, significantly lower than the bulk value of $1.10\ \text{Wm}^{-1}\text{K}^{-1}$. We are aware that bipolar effects can be disregarded at temperatures close to or below $300\ \text{K}$, meaning that the phonon thermal conductivity (κ_{lat}) can be calculated by subtracting the electronic thermal conductivity (κ_{ele}) from the total thermal conductivity (κ). To estimate κ_{ele} , we apply the Wiedemann-Franz law, which is expressed as $\kappa_{\text{ele}} = L\sigma T$. The Lorenz number, denoted by L , is determined by considering the scattering parameter and the measured Seebeck coefficient [32]. The calculated κ_{lat} for the $0.5\ \mu\text{m}$ and $1\ \mu\text{m}$ samples are roughly 0.14 and $0.18\ \text{Wm}^{-1}\text{K}^{-1}$, respectively, in the temperature range of 300 to $360\ \text{K}$. In contrast, the bulk material's κ_{lat} is roughly $0.70\ \text{Wm}^{-1}\text{K}^{-1}$. It is evident that the κ_{lat} of the film samples is significantly smaller than that of the bulk material. This ultra-low in-plane thermal conductivity is closely correlated with the



layered structure and preferred (015) orientation of the films, in addition to being related to several known defect patterns. The van der Waals gaps between the layers must be crossed by phonons, though not as extensively as along the c-axis. However, the average phonon mean free path is significantly reduced by this phonon interface scattering. According to molecular simulation studies by Mizuno et al., it is possible to achieve thermal conductivities lower than those of amorphous materials [33]. The key to this is effectively blocking the propagation of phonons, especially superlattice phonons. Mizuno et al. suggest that materials with extremely low thermal conductivities—beyond those of their amorphous counterparts—may be developed by introducing a significant mass difference between two interlayers or by weakening interactions at the interfaces between these layers [33].

4.1.6 Microstructures and Thermoelectric ZT of Films

High-resolution transmission electron microscopy (HRTEM) was used to analyze the representative microstructures of the 0.25 μm thick film, as illustrated in Fig. I.4.17. The HRTEM images demonstrate that the significant reduction in thermal conductivity is due to the effective scattering of phonons at the numerous and intricate interfaces within the nanostructures. These interfaces include mesoscale boundaries, planar defects, strain-induced distortions, and the formation of nano-moiré fringes. In physics,

moiré patterns are fascinating interference fringes produced by carefully superimposing a periodic template over another identical structure but with different displacements and twist angles. Ultralow thermal conductivity could result from the distribution of nanoscale moiré fringes, which would significantly increase the scattering of heat-carrying phonons..

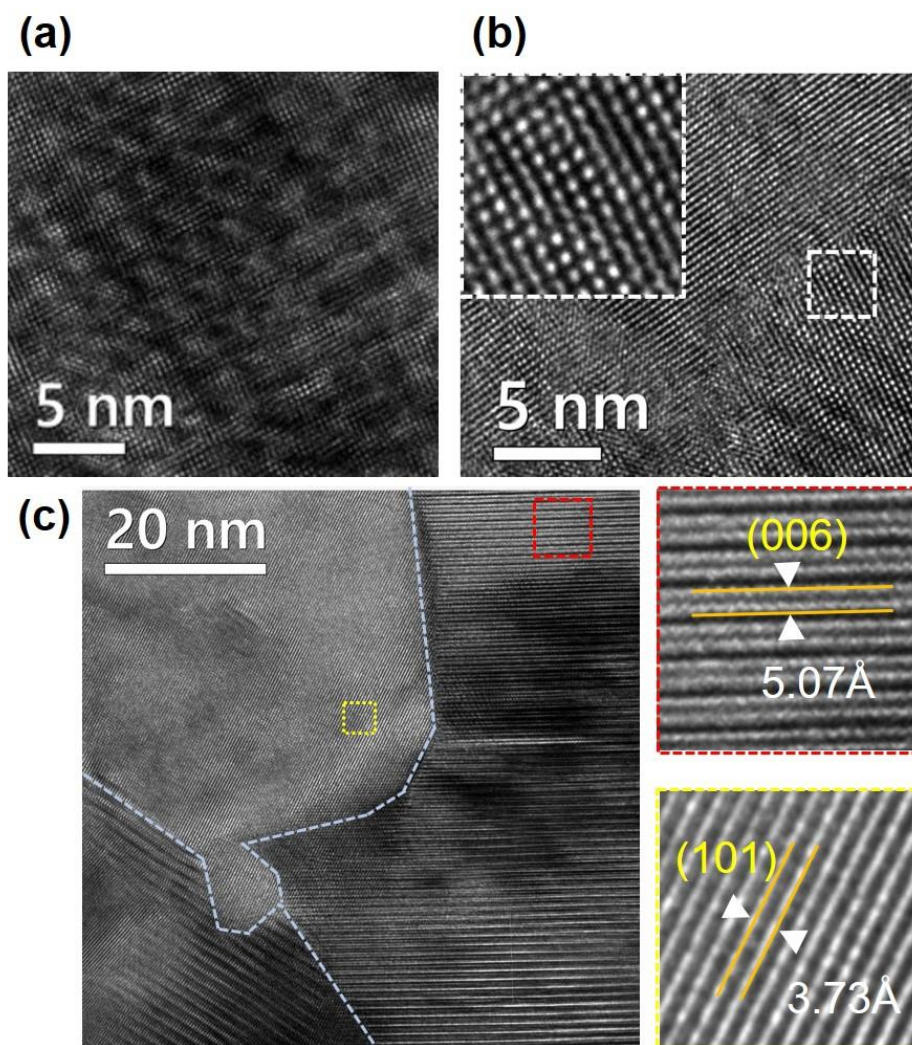
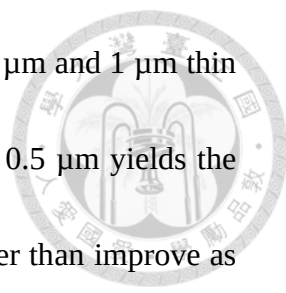


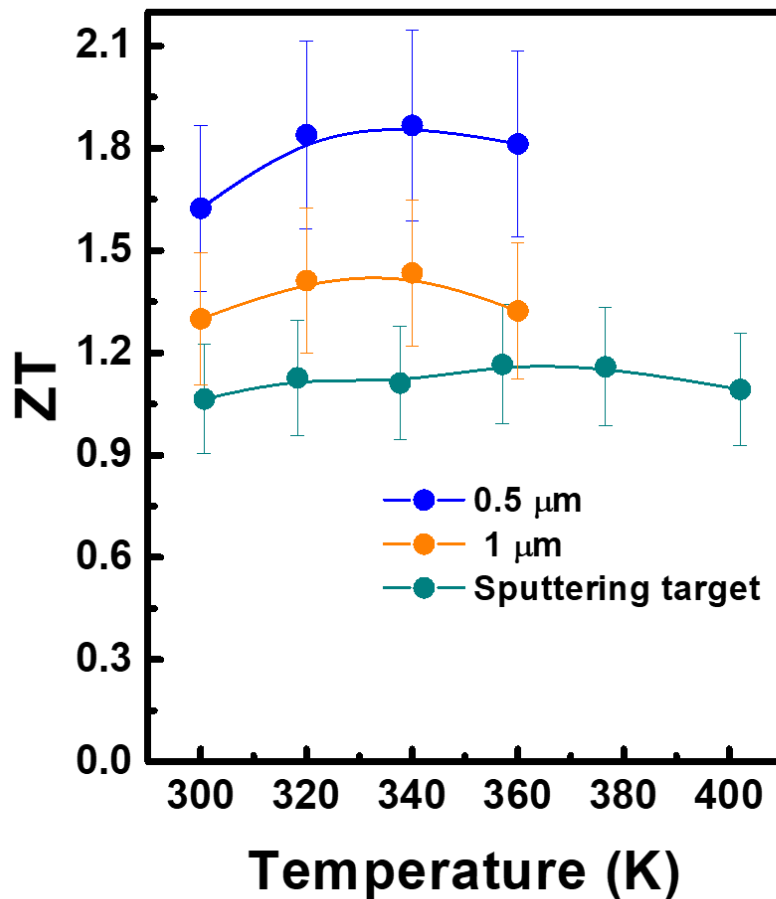
Fig.I.4. 17 (a)-(c) TEM analyses of the $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ film with thickness of 0.25 μm .



The calculated ZT values for the sputtering targets and the 0.5 μm and 1 μm thin film samples are displayed in [Fig. I.4.18](#). A thin film thickness of 0.5 μm yields the maximum ZT value of 1.86. However, the ZT values decrease rather than improve as the thickness increases beyond this threshold. The ZT is lower for the 1 μm thin film because its *PF* does not match that of the 0.5 μm sample, despite both samples having similar thermal conductivity. This pattern suggests that beyond an ideal threshold thickness, further increases lead to a decrease rather than an improvement in ZT values. This decrease in ZT is partly due to the *PF* inability to improve proportionately to the thermal conductivity at greater thicknesses. The exceptionally low thermal conductivity of the film is a major factor in achieving such high ZT values. Based on the HRTEM data, we hypothesize that phonons likely encounter multiple barriers as they propagate through the lattice, as shown in [Fig. I.4.19](#), leading to significant scattering. This scattering results in a low thermal conductivity of about $0.3 \text{ Wm}^{-1}\text{K}^{-1}$ [\[34\]](#).

The ZT values obtained for BST bulk [\[35\]](#), thin films [\[36\]](#), BT/single-walled carbon nanotube (SWCNT) [\[9\]](#), and superlattice (SL) thin films are comprehensively displayed in [Fig. I.4.20](#). BST thin films have a maximum ZT of approximately 0.89 [\[36\]](#). In comparison, the BT/BST SL [\[37\]](#) and BT/ZrB₂ SL [\[38\]](#) thin films perform better, with maximum ZT values of approximately 1.44 and 1.54, respectively. This outperforms the results from earlier research on films made of Bi–Sb–Te material

systems. Notably, Our investigation yielded a maximum figure of merit (ZT) value around 1.86 for 0.5 μm BST thin film sample, which is approximately 64% higher than that of bulk materials and roughly 24% higher than that of similar SL thin films. This accomplishment represents one of the best results reported for Bi_2Te_3 -based alloy thin films. To assess the repeatability of the thin film manufacturing process, we also conducted thermal and electrical performance cycling tests on several batches of samples. Our findings confirmed the exceptional thermal stability and reproducibility



of the thin film samples.

Fig.I.4. 18 ZT as a function of temperature

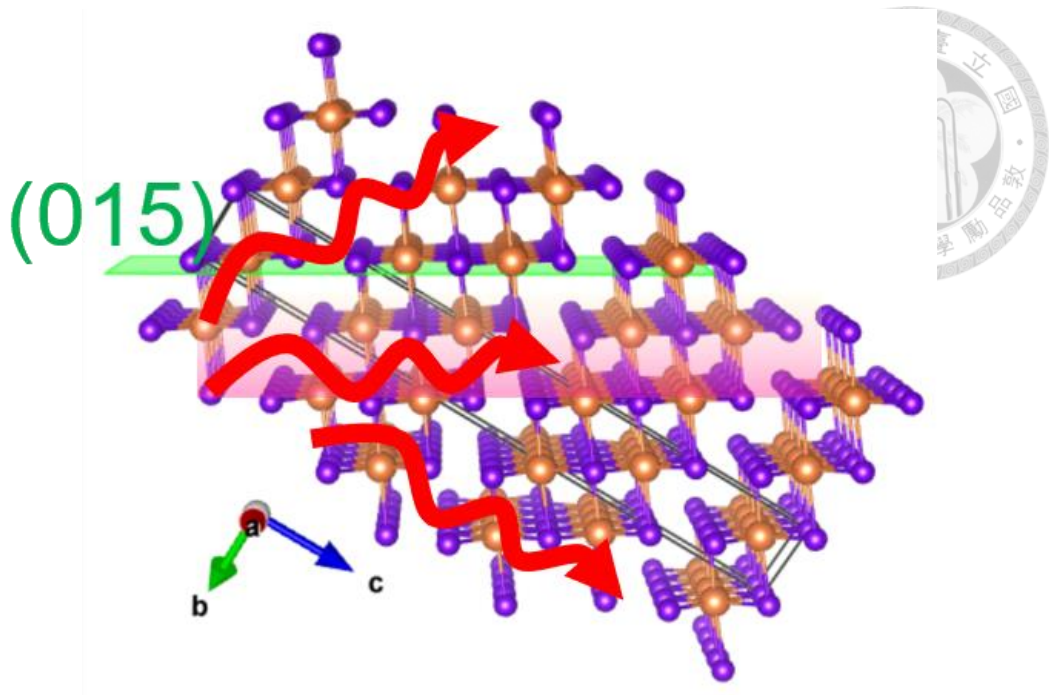


Fig.I.4. 19 Phonon propagation in the lattice structure

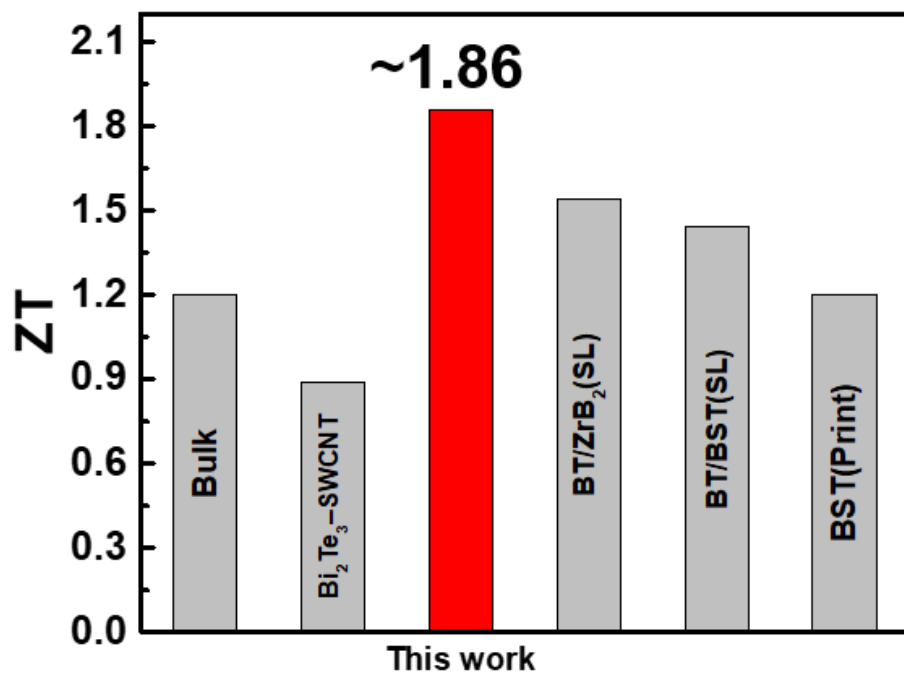
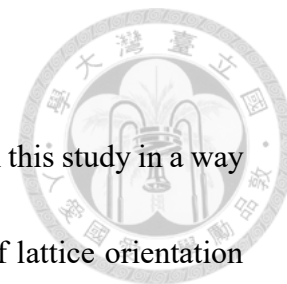


Fig.I.4. 20 ZT values for advanced p-type Bi_2Te_3 -based films and bulk materials.

Chapter 5 Conclusion



The thermoelectric properties of BST thin films are explored in this study in a way that has never been done before, with a focus on the importance of lattice orientation control and film thickness in improving thermoelectric performance. We successfully fabricated BST thin films of different thicknesses using RF sputtering and post-deposition annealing, and we systematically examined their structural, electrical, and thermal properties. Saturation annealing, a unique technique, resulted in a remarkable 450% increase in the PF , with the $0.5\ \mu\text{m}$ film reaching a PF of $18.1\ \mu\text{Wcm}^{-1}\text{K}^{-2}$ at 400 K. In addition, the paper presents an accurate in-plane thermal conductivity measurement technique based on the 3ω method, enabling the determination of an ultralow thermal conductivity of $0.3\ \text{Wm}^{-1}\text{K}^{-1}$ and a maximum ZT of 1.86 close to ambient temperature. These results highlight the significant influence that thickness and lattice orientation have on the thermoelectric efficiency of BST thin films, providing important insights for the development of high-performance thin-film thermoelectric generators. This work sets a new standard for thin-film thermoelectric materials and clarifies the mechanisms behind the enhanced thermoelectric capabilities of BST thin films, paving the way for their use in sustainable energy solutions.



**Part II. Novel Form of Topological Superconductivity
Arising from Inter-surface Electron Pairing in Sb_2Te_3
Nanoflakes**

Chapter 1 Introduction of Superconductivity and Topological Insulator



1.1 The Basic Principle of Superconductivity

Three distinct ideas about the behavior of electrical resistivity at zero temperature were proposed at the start of the 1900s. According to Matthiessen, resistivity is the sum of two components: one that depends on temperature and another that does not. As the temperature drops, resistivity would initially decline linearly, but it would eventually level off to a constant value. In contrast, Kelvin believed that as a metal approached absolute zero, electrons would become less mobile, turning the material into an insulator with infinite resistance. Lorentz's theory, on the other hand, is based on the idea that electron scattering is caused by ionic lattice vibrations. As these vibrations reduces, the electrons' mean free path lengthens, the resistivity approaches zero as the temperature nears absolute zero.

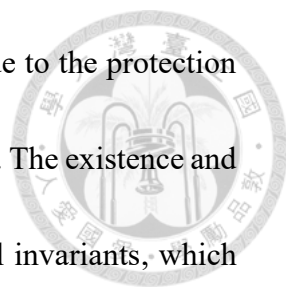
These theories were all shown to be false. It wasn't until Heike Kamerlingh Onnes discovered how to liquefy helium in 1908 that experiments at temperatures near absolute zero could be carried out. On April 8, 1911, he observed that the resistance of mercury vanished at temperatures below 4.2 K. He later found that there was no resistance at 7.2 K for lead and 3.8 K for tin when he conducted the same experiment

with each metal. He concluded that certain materials exhibit superconductivity, characterized by the abrupt disappearance of resistance at a critical temperature (T_c). Meissner and Ochsenfeld identified the second significant characteristic of superconductors in 1933. They discovered that the magnetic flux is expelled from the interior of a material when a superconductor is cooled below its critical temperature and placed in a weak magnetic field. Thus, within a few years, the two essential characteristics of superconductors were discovered:

1. Electrical transport: $\rho = 0$ for all $T < T_c$
2. No magnetic induction: $B = 0$ inside a superconductor

1.2 Introduction to Topological Insulator

Topological insulator (TI) is a material with unique electronic properties [39-42]. Although its interior is insulating, its surface or boundary is conductive. This property arises from the topological properties of the material rather than its chemical composition or crystal structure. These properties of topological insulators give them important application potential in fields such as electronics, quantum computing, and spintronics. The basic characteristics of topological insulators include internal insulation and surface conductivity. Its interior is insulating due to the energy gap formed by its electronic band structure, which prohibits electrons from moving freely within the bulk. Despite being insulating within the bulk, the surfaces or boundaries of

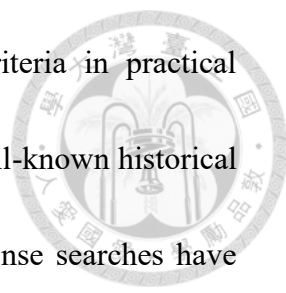


topological insulators can support conductive channels that exist due to the protection of time-reversal symmetry (TRS) and have spin-polarized properties. The existence and stability of surface states are protected by the material's topological invariants, which means that these states are stable against slight physical perturbations, such as impurities or defects. The concept of a topological insulator comes from the mathematical theory of topology. The theoretical basis of this material was first proposed by Kane and Mele in 2005 through research on graphene and further extended to three-dimensional systems by Moore, Balents, Fu, and Kane in 2006. They found that topological invariants can be used to describe the electronic structure of materials and predicted several possible three-dimensional topological insulator materials. Early experimental verification focused on the $\text{Bi}_{1-x}\text{Sb}_x$ alloy. Angle-resolved photoelectron spectroscopy (ARPES) technology was used to observe the surface states of these materials, confirming their topological properties. Subsequent experiments by Hsieh et al. and Nishide et al. further verified these results, demonstrating the unique electronic structure of topological insulators. Topological insulators have broad application prospects. First of all, the field of spintronics can use the spin polarization properties of their surface states to develop new spintronic devices and achieve more efficient electronic information processing. Secondly, in terms of quantum computing, the stability of the surface states of topological insulators and their analogy with the

quantum Hall effect make them potential components in quantum computing, helping to achieve more stable and reliable qubits. In addition, due to their sensitivity to external environmental perturbations, topological insulators can be used to develop highly sensitive sensors for detecting magnetic fields, electric fields, or other physical quantities. In summary, topological insulators are a new class of materials with revolutionary potential. Their unique electronic properties and stability make them broadly applicable in future technological developments.

1.3 Introduction to Topological Superconductivity

There are several proposals to realize topological superconductivity. Fu and Kane suggested that topological superconductivity could be achieved by the proximity of TI surface states to s-wave superconductors, where the surface Dirac cones are compelled to adopt a $p_x + ip_y$ pairing symmetry [43]. This concept was expanded to include the use of additional materials, such as semiconductors with spin-orbit interactions near s-wave superconductors and ferromagnetic insulators [44]. Despite significant experimental advancements in this direction [45-47], Majorana zero modes are confined to the interface between a TI and a superconductor, which limits experimental accessibility for manipulation. However, odd-parity pairing symmetry is typically required for materials to exhibit intrinsic topological superconductivity [48]. Still, it is



more challenging to satisfy the odd-parity superconductivity criteria in practical materials, making natural topological superconductors rare. The well-known historical contenders are superfluid ^3He [49] and Sr_2RuO_4 [50]. Recent intense searches have identified many additional candidates, often grown under pressure with excess Te. These include $\text{Cu}_x\text{Bi}_2\text{Se}_3$ [51,52], Bi_2Te_3 and Sb_2Te_3 at high pressure [53,54], $\text{In}_x\text{Sn}_{1-x}\text{Te}$ [55], $\text{Cu}_x(\text{PbSe})_5\text{Bi}_2\text{Se}_3$ [56], $\text{Sr}_x\text{Bi}_2\text{Se}_3$ [57], Tl_5Te_3 [58] and Sb_2Te_3 [59]. Although there is experimental evidence of unconventional superconductivity in these materials, unambiguous signatures of topological superconductivity have not been fully confirmed, partly due to potential alternative scenarios that could explain the experimental observations [60,61]. Therefore, establishing clear evidence of unconventional superconductivity is a vital first step.

Chapter 2 Materials Synthesis and Characterization

2.1 Synthesis Equipment

2.1.1 Three-zone tube furnace

The three-zone tube furnace is a high-temperature device commonly used in the preparation of materials, such as for processes like heat treatment, sintering, and annealing. It features three independently controlled temperature zones, allowing for

more uniform and precise temperature distribution throughout the tube. The furnace is composed of a cylindrical furnace tube, with a quartz tube diameter of 1 inch, capable of withstanding high temperatures and corrosion. Surrounding the tube are heating elements that provide the necessary heat. The exterior of the furnace is wrapped with insulation material to reduce heat loss. The three-zone design includes the front, middle, and rear zones, each with independent heating elements and temperature control systems, allowing for different temperature settings. Thermocouples and controllers monitor and adjust the temperature of each zone in real-time, ensuring stability and accuracy. The temperature of each zone can be adjusted according to different experimental needs, accommodating various materials.



Fig.II.2. 1 PVD system.

2.2 Experimental Equipment

2.2.1 X-Y-Z Micropositioner

The X-Y-Z micropositioner is a high-precision mechanical device used to accurately control and adjust the position of objects in three spatial directions. This device features three-axis control, with each axis representing a spatial direction (X, Y, and Z) that can be adjusted independently. The movement range of each axis depends on the design and application requirements. Precision operation is achieved through manual adjustments using fine-tuning knobs or screws, with a resolution of less than 1 micron.

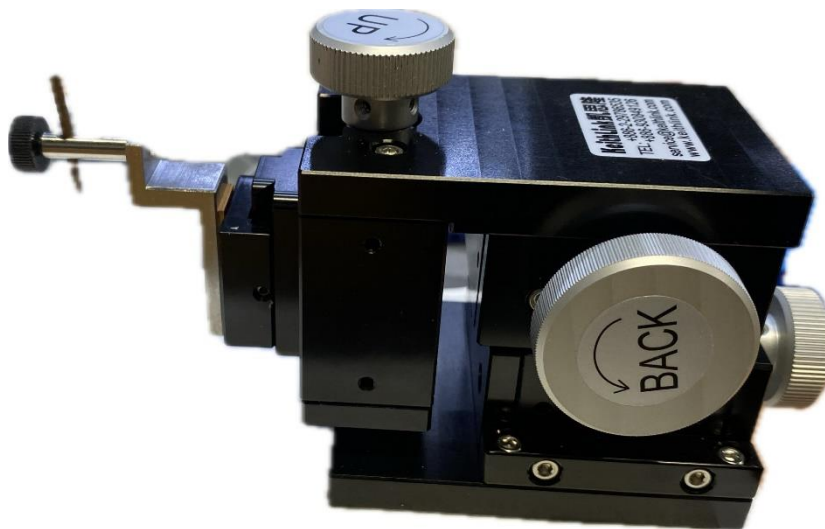


Fig.II.2. 2 Micropositioner.



2.2.2 Reactive Ion Etching

Reactive Ion Etching (RIE) is a plasma etching method used for precisely remove thin films or materials. RIE combines the advantages of physical and chemical etching, achieving high precision and selectivity. The basic principle involves using plasma-generated active ions and neutral particles to etch the material surface. During the reaction process, reactive gases (such as SF_6 , Ar, O_2 , etc.) are excited by a radio frequency (RF) electric field in the reaction chamber to form plasma. The ions in this plasma are accelerated by the electric field and vertically strike the material surface, performing physical etching. Simultaneously, the neutral particles from the reactive gases chemically react with the material surface, generating volatile byproducts and thus performing chemical etching. These volatile byproducts will be removed from the chamber by the vacuum pump, which will complete the etching process. By adjusting the reactive gases and the duration based on different materials and etching needs, this technique is commonly used for surface cleaning and the removal of residual

photoresist.



Fig.II.2. 3 Reactive ion etching

2.2.3 Electron Beam Lithography Writer

The Electron Beam Lithography Writer (E-Beam writer) is one of the high-precision fabrication tool primarily used for creating ultra-fine structures. The working principle of the EBeam writer involves using a focused electron beam to directly write patterns on an electron resist (electron-sensitive material). An electron gun generates a beam of high-energy electrons, which are accelerated and focused into an extremely fine beam, with an acceleration voltage of 30kV, typically with a diameter of just a few nanometers. Through electromagnetic lenses and deflection coils, the electron beam can

precisely scan and position on the surface of the resist, forming the desired pattern. The electron beam exposes the resist, altering its solubility. Depending on the type of resist (positive or negative), the exposed areas will either dissolve or remain intact during the subsequent development process. After exposure, the resist is developed to form precise nanoscale patterns.



Fig.II.2. 4 Electron beam lithography writer

2.2.4 Mask Aligner

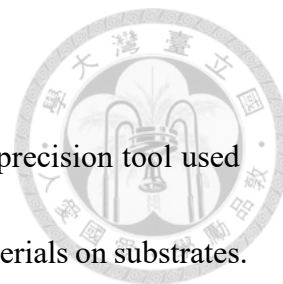
The Mask Aligner is a high-precision lithography tool primarily used for fabricating semiconductor devices, micro-electromechanical systems (MEMS), and other micro and nano structures. The system uses ultraviolet (UV) light to transfer

patterns from a photomask onto a photoresist, achieving precise pattern alignment and transfer. The basic principle of the Mask Aligner is as follows: First, the photomask is a non-transparent plate containing the desired pattern, made of glass with a coating of a non-transparent metal layer. Next, the photoresist is evenly applied to the substrate and prebaked to remove solvents. Then, using a microscope and alignment system, the pattern on the photomask is precisely aligned to the designated position on the substrate. Following this, a UV light source exposes the pattern through the photomask onto the photoresist, causing a chemical reaction in the exposed areas. After exposure, the substrate undergoes development to remove either the unexposed or exposed photoresist, forming the pattern. Due to its high precision, efficiency, and flexibility, the Mask Aligner is widely used in various micro and nano manufacturing fields.



Fig.II.2. 5 Mask aligner

2.2.5 Electron Beam Evaporator



The Electron Beam Evaporator (E-Gun Evaporator) is a high-precision tool used in vacuum coating technology, primarily for depositing thin film materials on substrates.

The E-Beam evaporator utilizes a high-energy electron beam generated by an electron gun to heat and evaporate the target material. The process works as follows: the electron gun emits high-energy electrons, which are accelerated and focused into an electron beam. This beam is directed onto the surface of the target material, where the kinetic energy of the electrons is converted into thermal energy, rapidly heating the target. When the target material reaches its evaporation point, it transforms into a gaseous state. The evaporated material molecules travel through the vacuum chamber and condense on the cooled substrate surface, forming a uniform thin film. Its advantages include high purity, as the deposition takes place in a high vacuum environment, resulting in films with high purity and low impurity content. Additionally, the evaporation rate and film thickness can be precisely controlled.



Fig.II.2. 6 Electron beam evaporator

2.3 Measurement Equipment and Techniques

2.3.1 Atomic Force Microscope

Recognized for its capacity to resolve surfaces at the atomic level, the Atomic Force Microscope (AFM) is a high-resolution microscopy technique used to image and quantify the topography and physical characteristics of sample surfaces. The interaction between a probe and the sample surface is the foundation of the AFM's operation. Its

fundamental components and mode of operation are as follows: The AFM uses an incredibly sharp probe mounted on a flexible cantilever. The probe's tip radius can be as small as a few nanometers. When the probe comes into contact with or approaches the sample surface, the cantilever experiences minute deflections due to atomic interactions between the two. A position-sensitive detector (photodiode array) receives a laser beam directed at the behind of the cantilever. As the cantilever deflects, the position of the reflected laser changes, allowing for the measurement of the forces interacting between the probe and the sample surface. By laterally scanning the probe and recording the variations in contact force at each point, the AFM can generate a three-dimensional topographic map of the sample surface.



Fig.II.2. 7 Atomic force microscope

2.3.2 Measurement chip

The measurement chip used in this research is designed according to our own requirements, and the designed patterns are fabricated using photolithography technology. First, a silicon (Si) wafer with a silicon dioxide (SiO_2) thin film is coated with photoresist by spin coating. Then, the photoresist is exposed to ultraviolet light with the contact pad pattern. After exposure, the soluble photoresist is developed by the developer. The wafer is then placed in a RIE system, where the residual photoresist in the developed areas is removed by reactive ions. Subsequently, chromium/gold (Cr/Au) is deposited using an evaporator, and the photoresist is removed with acetone. After the lift-off process is completed, the measurement chip is ready for use.

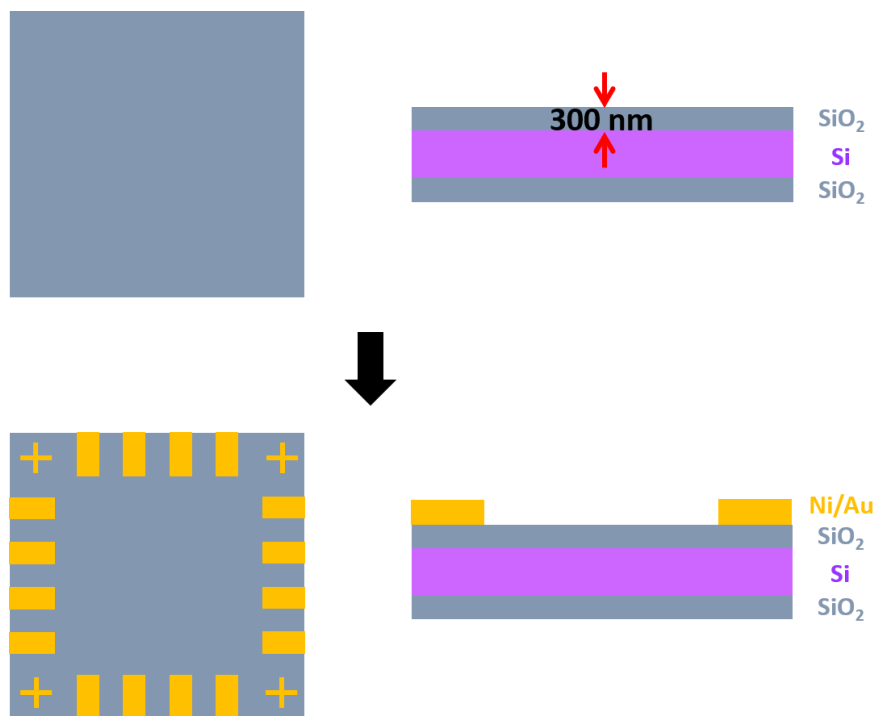


Fig.II.2. 8 Measurement chip

2.3.3 Four-probe method

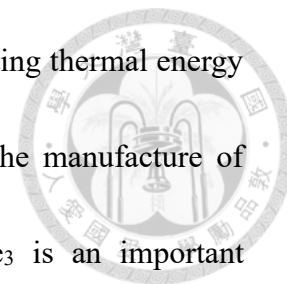


The four-probe method is a precise technique used to measure the resistivity of materials. This method measures the resistance of a sample using four independent probes, thereby avoiding the influence of contact resistance on the measurement results. The basic principle of the four-probe method is as follows: four probes are arranged in a straight line at equal intervals and gently contact the surface of the sample. The outer two probes (current probes) are used to apply current, while the inner two probes (voltage probes) are used to measure the voltage. As the current flows through the sample, a voltage drop is generated between the inner probes, which is related to the resistance of the sample. Based on the current and voltage drop, the resistivity of the sample is calculated using the appropriate formula.

Chapter 3 Introduction of Sb_2Te_3 Materials

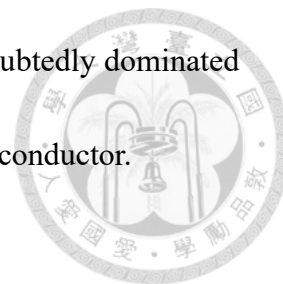
Sb_2Te_3 (antimony telluride) is a binary compound composed of antimony (Sb) and tellurium (Te), exhibiting various significant physical and chemical properties. Its crystal structure is layered, belonging to the trigonal crystal system, with two-dimensional layered characteristics formed by Sb-Te and Te-Te bonds, where the layers interact through van der Waals forces. Sb_2Te_3 is widely used in thermoelectric materials

due to its excellent thermoelectric performance, effectively converting thermal energy into electrical energy, or vice versa, and is commonly used in the manufacture of thermoelectric modules and thermocouples. Additionally, Sb_2Te_3 is an important material for the study of topological insulators.



In this study, we discovered that these superconductors are formed through the pairing [43] of surface electrons on Sb_2Te_3 nanosheets. Previously, bulk Sb_2Te_3 grown by furnace melting was known to exhibit superconductivity at approximately 9K. In this work, we identified another type of superconductivity in Sb_2Te_3 nanosheets, different from the 9K superconductivity, which becomes superconducting at $T_c < 2\text{K}$ only when the thickness is less than 9 quintuple layers (QLs). Specifically, we found that the superconductivity of Sb_2Te_3 nanosheets depends on the thickness range and manifests in two distinct forms. When the thickness exceeds 11QLs, this superconductivity is of the same type as the surface superconductivity found by Zhao et al., but with a smaller Fermi surface in the Sb_2Te_3 nanosheets. When the thickness is below 11QLs, a new type of superconductivity begins to form from 9QLs and reaches its maximum around 6QLs, at which point the Dirac cones on the top and bottom surfaces start to mix. Experimental data and theoretical analysis indicate that the superconductivity [44-48] in nanosheets originates from the pairing of two surface Dirac fermions, contrasting with the single-surface superconductivity found by Zhao et al. Our results suggest that

the pairing symmetry based on surface Dirac cone coupling is undoubtedly dominated by spin $p_x + ip_y$ pairing, forming a new class of topological superconductor.



Chapter 4 Sample synthesis and Characterization

4.1 Nanoflake crystal growth

The growth mechanism of Sb_2Te_3 nanoflakes is achieved using the Physical vapor deposition (PVD) method. This technique involves transferring raw materials from the source zone to the deposition zone through high-temperature gas-phase reactions. First, high-purity Sb_2Te_3 powder is placed in the source zone of a quartz tube. A silicon dioxide (SiO_2) substrate is placed in the deposition zone. The quartz tube is then sealed and evacuated to ensure an oxygen-free environment. By controlling the temperatures in different regions of the quartz tube, a temperature gradient is established, with the source zone typically heated to 600°C and the deposition zone maintained at approximately 300°C . Argon gas is introduced to transport the evaporated source materials (Sb_2Te_3) from the source zone to the deposition zone. In the deposition zone,

the vapor condenses on the substrate surface, forming Sb_2Te_3 nanoflakes.

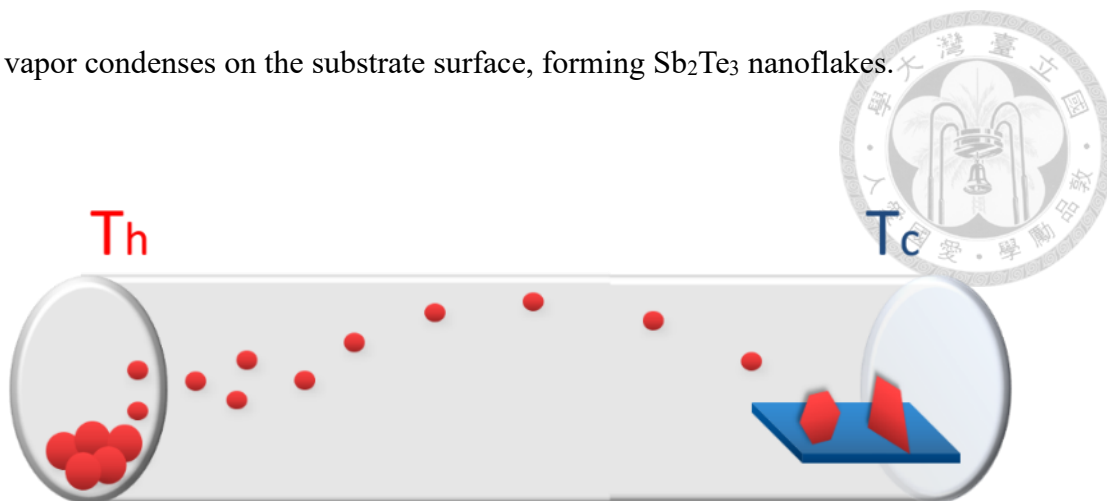


Fig.II.4. 1 PVD Schematic diagram

4.2 Sample preparation, characterization and measurement

In this study, we measured single crystalline Sb_2Te_3 nanoflakes of varying thicknesses. Two batches of single crystalline Sb_2Te_3 nanoflakes (NFs) with thicknesses of 5-9 quintuple layers (QLs) (Batch A) and 11-27 QLs (Batch B) were synthesized on substrates using the PVD method, with Sb_2Te_3 as the source material. SEM images of several nanoflakes show that some are standing vertically while others are lying flat on the substrate. High-resolution TEM (HRTEM) analysis indicates that these nanoflakes are single crystals. Selected area electron diffraction (SAD) shows the hexagonal lattice of the ab-plane.

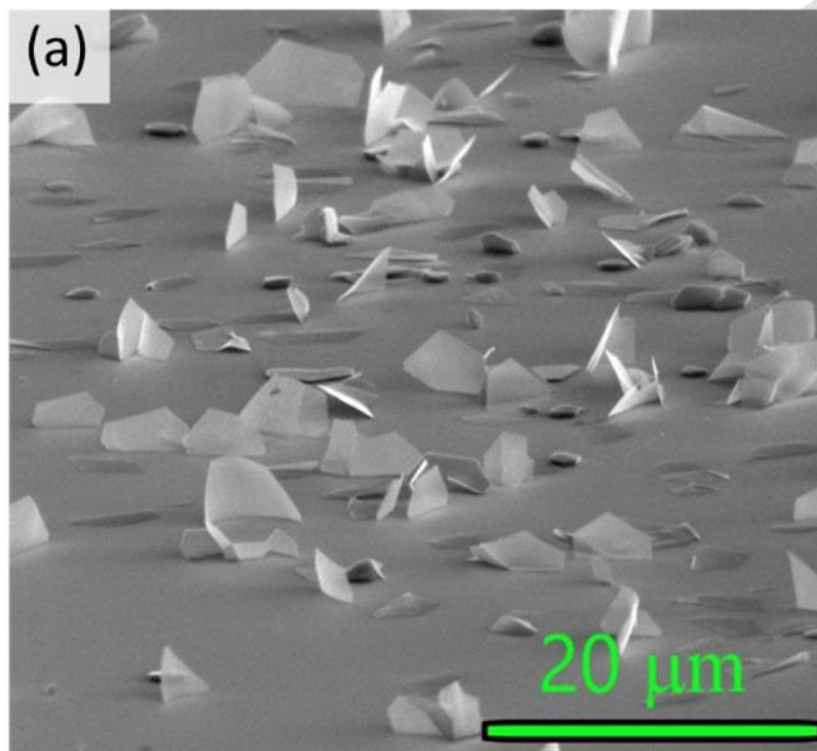


Fig.II.4. 2 SEM image of nanoflakes on Si/SiO₂ substrate.

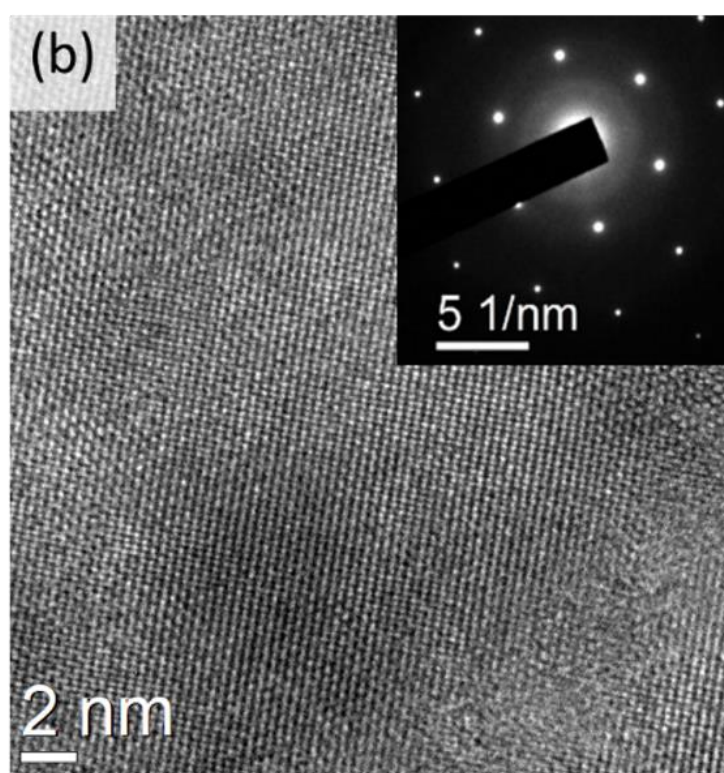


Fig.II.4. 3 TEM image of nanoflake and SAED

And the sharp diffraction pattern indicates the high crystalline quality of these nanoflakes. Energy-dispersive X-ray spectroscopy (EDX) mapping demonstrates the uniform distribution of Sb and Te elements, with an atomic ratio of Sb/Te being $(40\pm1)/(60\pm1)$. To conduct transport measurements, selected nanoflakes were transferred to a homemade 16-terminal platform using a micromanipulator, followed by e-beam lithography patterning to create electrodes. The nanoflake NF9, equipped with electrodes and leads for four-probe measurements, was used. The thickness of the nanoflakes was measured by AFM, and the thickness profile of NF9 shows an average thickness of 9.6 ± 0.4 nm. The electrical resistivity of nanoflakes from Batch A and Batch B was measured as a function of temperature.

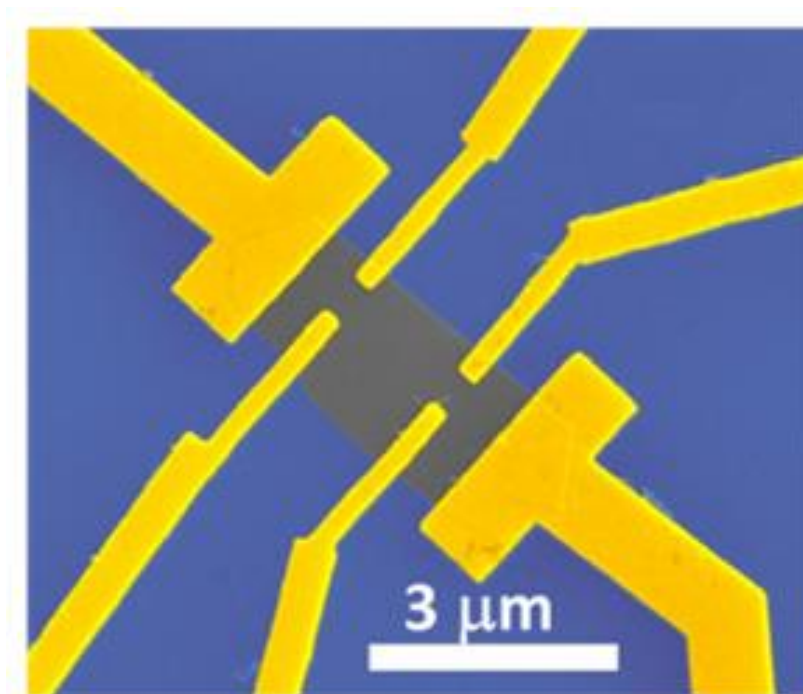


Fig.II.4. 4 Nanoflake NF9 with gold electrodes

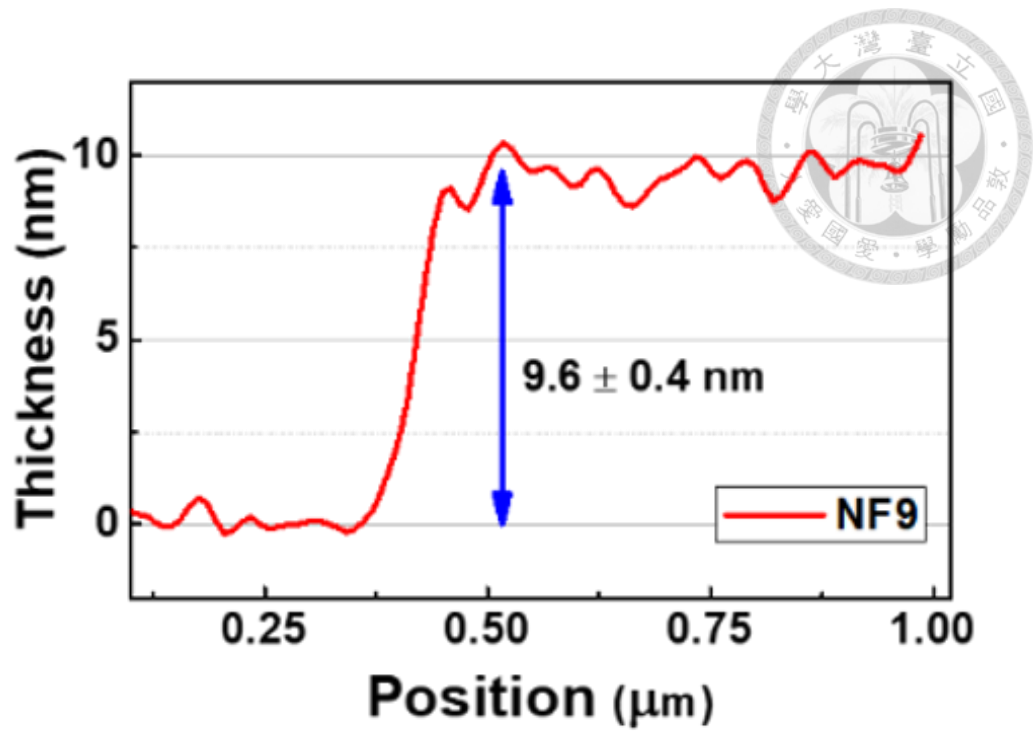


Fig.II.4. 5 Thickness profile of NF9 taken by AFM

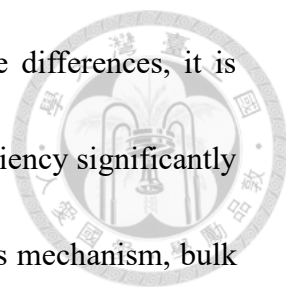
All samples exhibited metallic behavior in the normal state. Generally, the resistivity is inversely proportional to the carrier density, which increases as the Fermi energy increases. On average, the electrical resistivity of Batch B nanoflakes is much lower than that of Batch A, indicating a larger Fermi energy (defined as the energy difference between the Dirac point and the Fermi surface) for Batch B samples. This can be understood by noting that the deficiency of Te strongly affects the hole concentration in p-type Sb_2Te_3 [59, 63, 64], making the carrier density and electrical resistivity of Sb_2Te_3 very sensitive to the Te atmosphere during the growth process [59]. Lower Te vapor pressure in the growth tube results in higher resistivity due to a smaller

Fermi surface.

4.3 Characterization of Transport Properties



We investigated the temperature dependence of the electrical resistivity of Sb_2Te_3 nanoflakes (NFs) and bulk crystals using Quantum Design PPMS and a ^3He cryostat. [Fig.II.4.6b](#) shows the temperature-dependent resistivity of Batch B samples, specifically 11-, 12-, 16-, 17-, 19-, and 27-QLs NFs. These samples exhibit characteristics of topological insulators, where thinner NFs demonstrate lower resistivity. This phenomenon can be attributed to the dominance of surface states in thinner NFs, which have a larger surface-to-volume ratio. Superconducting transitions were clearly observed in NF11 and NF12, with transition temperatures T_c of 2.2 K and 2 K, respectively (see insets of [Fig.II.4.6b](#) and [Fig.II.4.11](#)). However, the superconducting transition becomes difficult to observe in thicker samples like NF16 and NF17, and no signs of superconductivity are found in samples with thickness $d \geq 27$ QLs. Similarly, the temperature dependence of the resistivity for Batch A samples (5-, 7-, and 9-QLs NFs) is shown in [Fig.II.4.6a](#). Significant drops in resistivity at low temperatures were observed in NF5 and NF7, indicating transition temperatures near 1.27 K and 1.51 K, respectively (see inset of [Fig.II.4.6a](#)). In contrast, NF9 exhibited only a slight resistivity drop near 0.6 K, suggesting weak superconducting fluctuations that do not result in a full superconducting transition. Despite both batches of NFs



displaying superconductivity, their origins differ. To explore these differences, it is important to note that, as mentioned previously, tellurium (Te) deficiency significantly impacts the electrical resistivity of the Sb_2Te_3 system. To verify this mechanism, bulk crystals were grown using the furnace melting method with volume-controlled techniques. Even small variations in Te vapor pressure can cause a wide range of resistivity distributions at a fixed temperature, illustrating the presence of surface states. This observation is consistent with the composition and deficiency sensitivity characteristics of Sb_2Te_3 reported by Zhao et al.. In addition to its sensitivity to Te vapor pressure, the resistivity of Sb_2Te_3 nanoflakes also shows a strong dependence on thickness. The resistivity or conductivity observed in experimental measurements depends on the ratio of the surface state to the total volume of the sample. When the top and bottom surface states do not overlap, the conductivity is given by

$$\sigma = 2\sigma_s \frac{\xi_d}{d} + \sigma_b \quad (1)$$

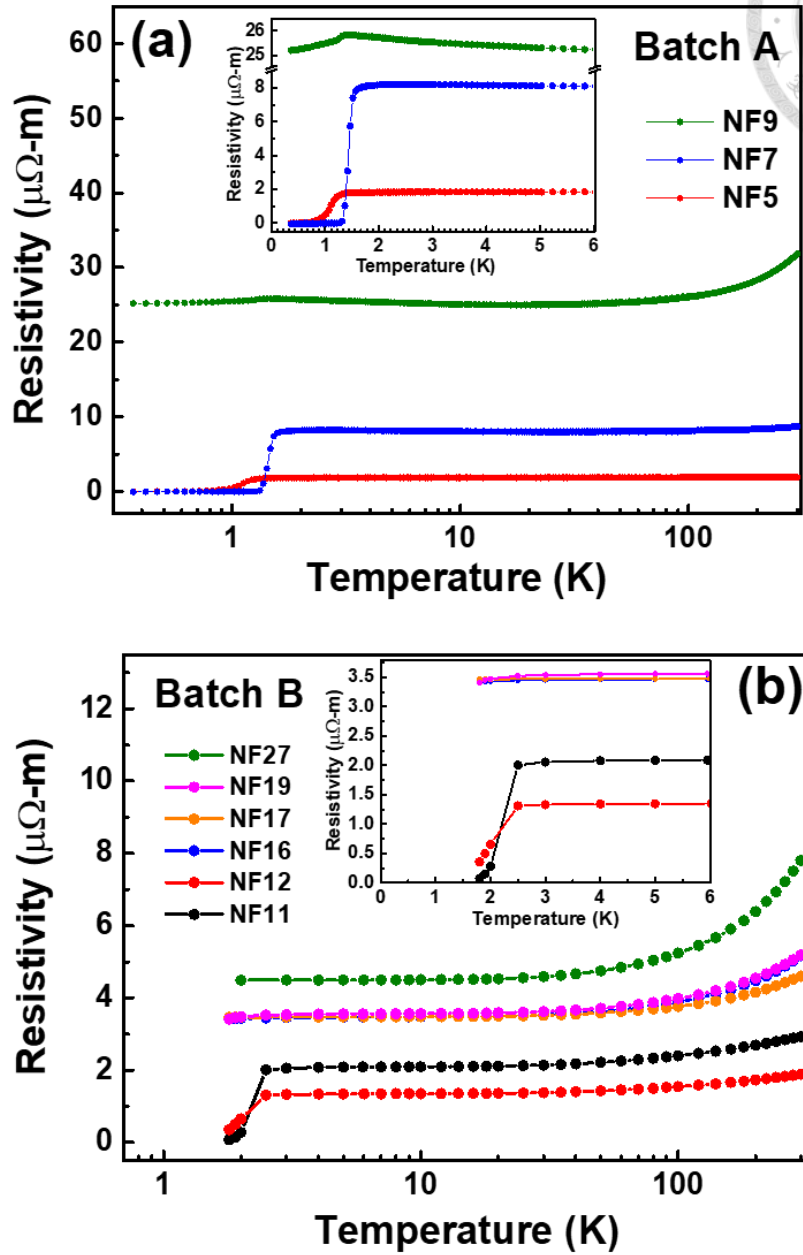
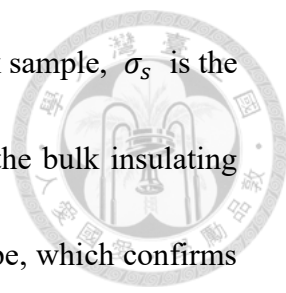
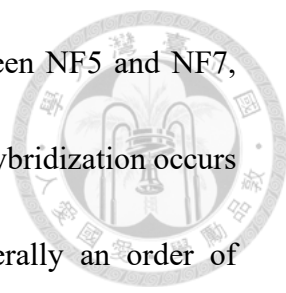


Fig.II.4. 6 (a) and (b) are the temperature dependence of electrical resistivity of Sb_2Te_3 nanoflakes of Batch A and Batch B respectively. Inset: Enlarged plot of the electrical resistivity at low temperatures.



where ξ_d is the decay length of the surface states into the bulk sample, σ_s is the conductivity of the surface states, and σ_b is the conductivity for the bulk insulating state. All Batch B samples show $1/d$ dependence with the same slope, which confirms that the transport properties of Batch B samples are dominated by non-overlapped surface states with the same Fermi energy. This is also consistent with the crossover behavior of the surface state dispersion of ARPES observed in Bi_2Se_3 [65] and Sb_2Te_3 [62]. Hence, we conclude that the Dirac surface states of top and bottom surfaces do not have appreciable overlap for Batch B samples. The observed superconductivity can be thus attributed to occur in individual surface Dirac cone and belongs to the same superconducting class observed in bulk Sb_2Te_3 . However, since the normal state resistivity of Batch B samples is at least twice larger than that ($0.6\mu\Omega - m$) of bulk Sb_2Te_3 grown by furnace melting method, the charge carrier density is smaller and hence the transition temperature is less than 9K. On the other hand, Batch A samples exhibit completely different transport properties. The conductivity starts to deviate from linear behavior, indicating that the transport properties of Batch A samples are dominated by overlapped surface states. In this case, the surface states overlap, and the conductivity measured from current and voltage depends on the detailed current distribution. Therefore, the ratio of the decay length to thickness, $2\xi_d/d$, in Eq.(II.1) is replaced by an enhancement factor, $s(d)$, to account for the current distribution.



Notably, there is a significant change in current distribution between NF5 and NF7, with the ratio $s(d = 5)/s(d = 7) \sim 4.5$. This reflects the fact that hybridization occurs in the NF5 sample. The resistivity in Batch A samples is generally an order of magnitude larger, indicating an even smaller Fermi energy compared to Batch B samples. [Fig.II.4.6 a](#) shows that superconductivity in Batch A samples begins at 9 QLs with a transition temperature $T_c \approx 0$ and reaches a maximum of 1.52 K near 7 QLs. Since the surface Dirac cones on the top and bottom surfaces start to hybridize, this suggests that the superconductivity in Batch A samples originates from the coupling of inter-surface Dirac cones. Moving forward, we will focus on analyzing Batch A samples.

4.4 Shubnikov-de Haas Oscillations and Surface Dirac Cone States

The Landau levels (LL) observed in Shubnikov-de Haas (SdH) oscillations are one of the most direct probes of quasiparticle excitations in metals. These oscillations provide direct evidence of surface Dirac cone states and information about the Fermi energy (E_F) in Sb_2Te_3 nanoflakes. In the inset of [Fig.II.4.7b](#), the SdH oscillation is clearly shown in the field dependence of the electrical resistivity in NF9. Arrows indicate the locations of oscillations that are present at all temperatures, while other oscillation-like features not present at all temperatures are not considered signals of

quantum oscillations. Using the semi-classical Onsager equation [66, 67]:

$$2\pi(n + \gamma) = S_F \frac{\hbar}{eB} \quad (2)$$

where S_F is the cross section of the Fermi surface (FS), n is the LL index, e is the electron charge, γ is the Berry phase, and B is the magnitude of the magnetic field, we determined S_F and γ . We found $S_F=18.8$ and $\gamma=0.65$. The value of γ being close to $1/2$ indicates that the surface state of NF9 is roughly a massless Dirac fermion. Additionally, the resulting Fermi wave vector k_F is found to be $0.024 \text{ \AA}^{-1}$, which is smaller than the $k_F \approx 0.0347 \text{ \AA}^{-1}$ of the surface state in bulk Sb_2Te_3 as reported by Zhao et al. [59], consistent with conclusions based on resistivity measurements at zero field.

To calculate the Fermi level distance E_D from the Dirac Point, we adapt the Fermi velocity as $v_F \sim 4 - 5 \times 10^5 \text{ m/s}$ which is derived from the surface state dispersion of ARPES [62,68]. The corresponding Fermi level distance would be in range of $E_D = 64 \sim 80 \text{ meV}$. Further analysis is performed to confirm the presence of surface Dirac cones by examining the weak anti-localization effect. This is done by first subtracting a classical background contribution $G_c = 1/(R_0 + R_1 B)$ [69,70]. In the weak field limit when the magnetic length is much larger than the elastic scattering length, the deviation of the residual conductance due to quantum correction, $\Delta G = G(B) - G(0)$, is then fitted by using the Hikami-Larkin-Nagaoka (HLN) model [67, 71],

$$\Delta G = -\frac{\alpha e^2}{2\pi^2 \hbar} \left[\ln \left(\frac{\hbar}{4eL_\phi^2 B} \right) - \psi \left(\frac{1}{2} + \frac{\hbar}{4eL_\phi^2 B} \right) \right] \quad (3)$$

where α is a dimensionless parameter determined by the number of conduction channels and the strength of the spin-orbit coupling, ψ is the digamma function, and L_ϕ is the effect coherent length. As shown in [Fig.II.4.7a](#), the magneto conductance clearly exhibits weak anti-localization behavior. Furthermore, we find that the phase coherence lengths of NF5, NF7 and NF9 are 68, 178, and 57 nm, respectively, whereas the fitted pre-factors α are -0.96, -0.97, and -1.37 for NF 9, NF7, and NF5 respectively, in consistent with the presence of two Dirac cones in top and bottom surfaces [\[62\]](#). The measured weak anti-location effect in together with the quantum SdH oscillations thus confirm the presence of two surface Dirac cones with k_F being $0.024 \text{ \AA}^{-1}$.

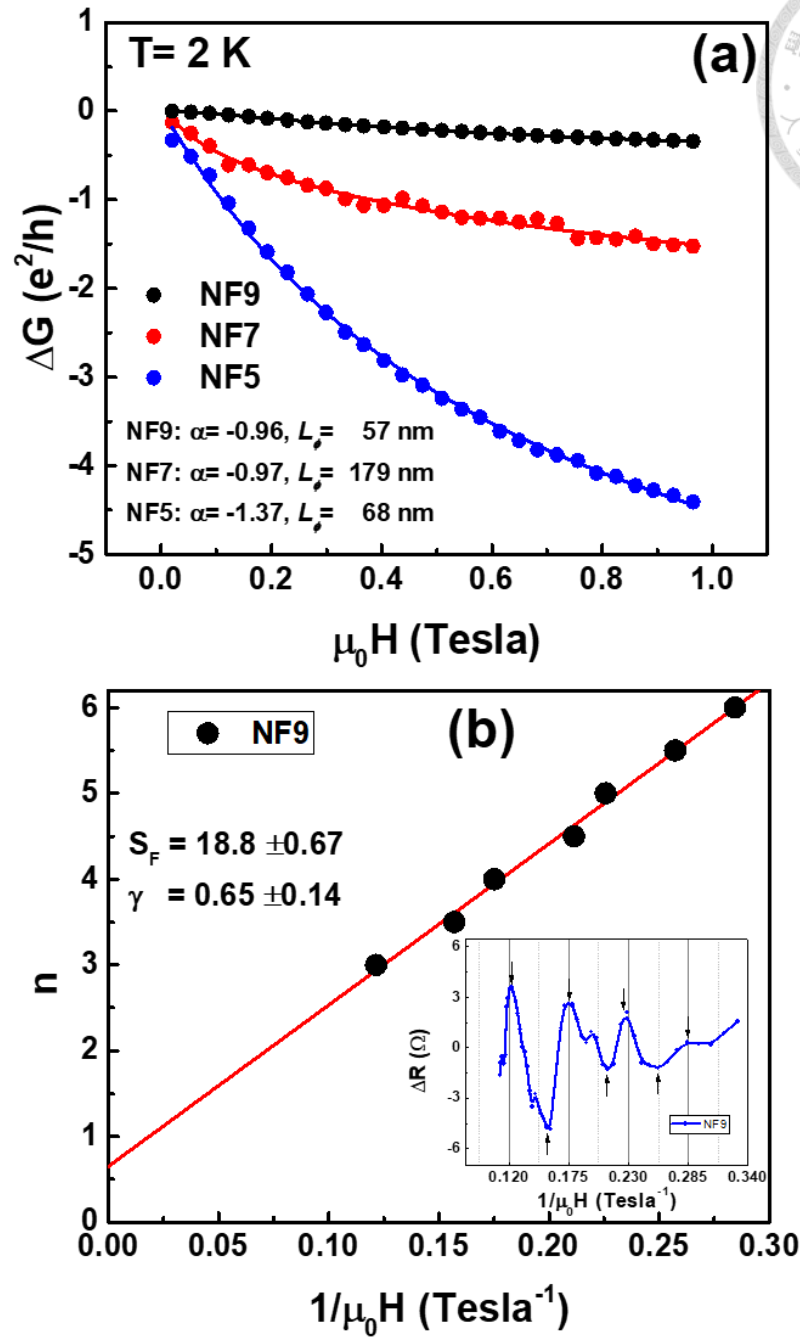


Fig.II.4. 7 (a) (b) are magnetic field dependent transport properties that illustrate the existence of surface states

4.5 Magnetic phase diagram and transport properties in B fields



The temperature dependence of resistivity for NF5, NF7 and NF9 under magnetic fields was performed to investigate the breaking and pairing symmetry of superconductivity. In perpendicular fields ($H_{c2}^{\perp}$), both NF5 and NF7 present a drastic shifting of superconducting transition to lower temperatures as magnetic field increases up to 2 T and 1T respectively. The estimated perpendicular upper critical field (determined by the onset of decreasing resistivity) for NF5 and NF7 at zero temperature are about 2 T, and 1 T respectively. For NF9, the resistivity bending (a trace of superconductivity) near 1.3 K is quickly suppressed by magnetic field of 0.5 T, showing a relatively weak superconducting transition in NF9. The temperature dependence of resistivity for NFs of Batch B under magnetic fields shows similar pair breaking effects. On the other hand, for fields in parallel to the surface of nanoflakes, the observed upper critical field $H_{c2}^{\parallel}$ is much larger than $H_{c2}^{\perp}$. The in-plane critical fields $H_{c2}^{\parallel}$ for Batch B samples (represented by NF11) exhibit steep curvature near T_c . It shows that for Batch B samples, the extrapolated $H_{c2}^{\parallel}(0)$ (~ 12 T) is much less than the estimated $H_{c2}^{\parallel orb}(0)$ based on the orbit effects. Hence the in-plane upper critical fields of Batch B samples at zero temperature are driven by the paramagnetic limit, which implies that there is singlet pairing component in Batch B samples. On the other hand, for Batch A

samples (represented by NF5), there is no steep curvature observed near T_c . The extrapolated $H_{c2}^{\parallel}(0)$ is larger than the estimated $H_{c2}^{\parallel orb}(0)$. It is thus expected that $H_{c2}^{\parallel}(0)$ is determined by the orbit effects, which indicates that Batch A samples are dominated by the triplet pairing.

The field-dependent resistivity of NF5, NF7 and NF9 under magnetic fields represent the breaking of superconductivity by magnetic fields (Fig.II.4.12). The electrical transport properties in the presence of magnetic fields are performed in the ^3He -insert with a low frequency (9.7 Hz) AC excitation. Fig.II.4.12 and Fig.II.4.13 present results of measurements at 0.3 K. Fig.II.4.12 shows the normalized resistivity R/R_{9T} , where R_{9T} is the resistivity at 9 Tesla. The normalization of resistivity to R_{9T} removes effects due to the weak anti-localization effects observed in Fig.II.4.7a. NF5 and NF7 both shows clear superconducting transition that their resistance drops to zero at absence of magnetic field, while the NF9 shows a mild resistivity drop around 0.3 Tesla. The arrows in Fig.II.4.12 indicate locations of the critical fields H_{C2} at 0.3 K, and they are determined as 1 and 0.8 Tesla for NF5 and NF7 respectively, which shows the strong increase of H_{C2} as d decreases. Meanwhile, an in-situ current dependent measurements were also performed by DC excitation with so-called bias compensation technique to study the behavior of current dependent pair breaking. The results indicate that the superconductivity was suppressed by increasing of excitation current in NF5 and NF7,

and their critical currents density J_C are determined by the inflection point of that in first transition (arrows in [Fig.II.4.13](#)) as 5×10^8 and 0.93×10^8 A/m², respectively. Combining results of H_{C2} and J_C indicates that they have the same thickness-dependence ([Fig.II.4.14](#)).

The strong thickness-dependent magnetic properties have the same origin from the hybridization of inter-surface Dirac cones. The perpendicular upper critical $H_{C2}^\perp$ is determined by the orbit effect when vortices overlaps and is given by $H_{C2}^\perp = \phi_0/2\pi\xi^2$ [73] with ϕ_0 being the flux quantum and ξ being the effective coherence length at zero temperature. In presence of disorders, $\xi = 0.885\sqrt{\xi_0\ell}$ with ξ_0 being the coherent length of clean system ($\xi_0 = \hbar v_F/\pi\Delta$) and ℓ being mean free path. Since the gap function Δ is proportional to T_C , the increase of ξ_0 from NF7 to NF5 is approximately given by the ratio of T_C . When top and bottom surface states start to overlap, the mean free path ℓ is limited by thickness and can be estimated by d . The ratio of H_{C2} (NF5) to H_{C2} (NF7) is thus given by $T_C(\text{NF5})/T_C(\text{NF7}) \times 7/5 \sim 1.17$, which agrees with the ratio obtained in [Fig.II.4.14](#). The enhancement of H_{C2} for small d can be thus attributed to the hybridization of inter-surface Dirac cones and the inter-surface pairing. On the other hand, the critical current density J_C is limited by the self-generated magnetic flux at surfaces that enters the sample [74]. When the penetration depth at zero temperature satisfies $\lambda(0) \sim d$, the current distribution is uniform and critical

current density is given $J_C \sim H_{C1}/d$ with H_{C1} being the lower critical field. As explained in previous sections, the enhancement factor due to hybridization for the current distribution between NF7 and NF5 is $s(d = 5)/s(d = 7) \sim 4.5$. Hence the change of the critical current density J_C from NF7 to NF5 is roughly $s(d = 5)/s(d = 7) \sim 4.5$ (H_{C1} depends on the penetration depth $\lambda(0)$, which is roughly independent of d), in agreement of the ratio obtained in Fig.II.4.14.

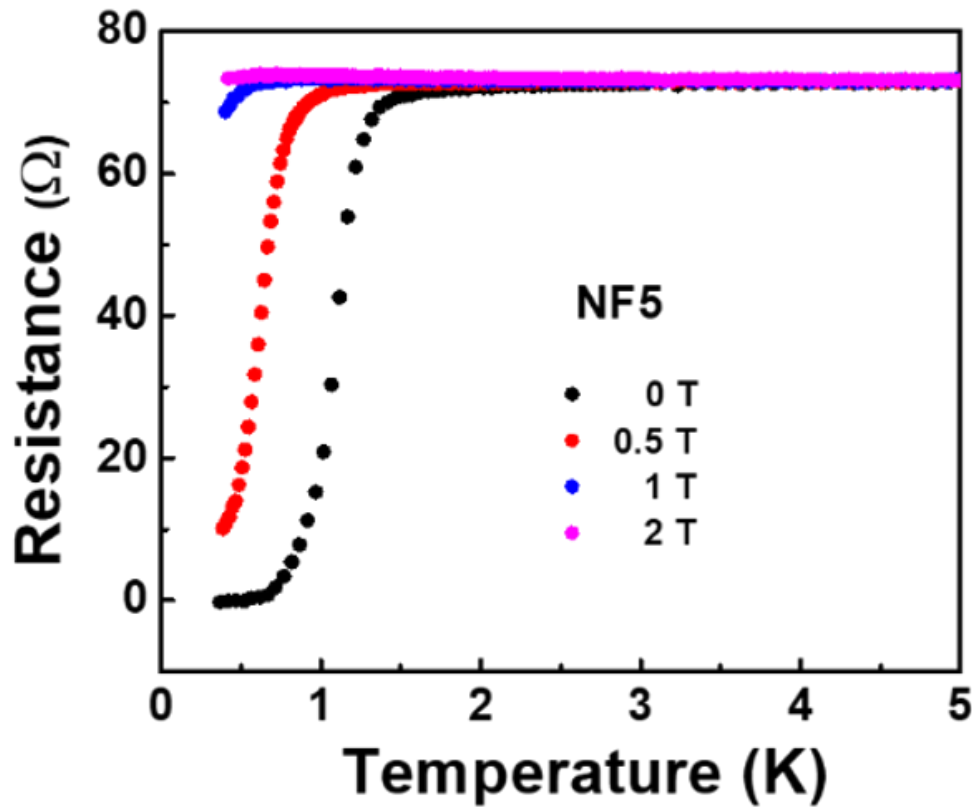


Fig.II.4. 8 The NF5 temperature dependent transport properties at various perpendicular magnetic fields.

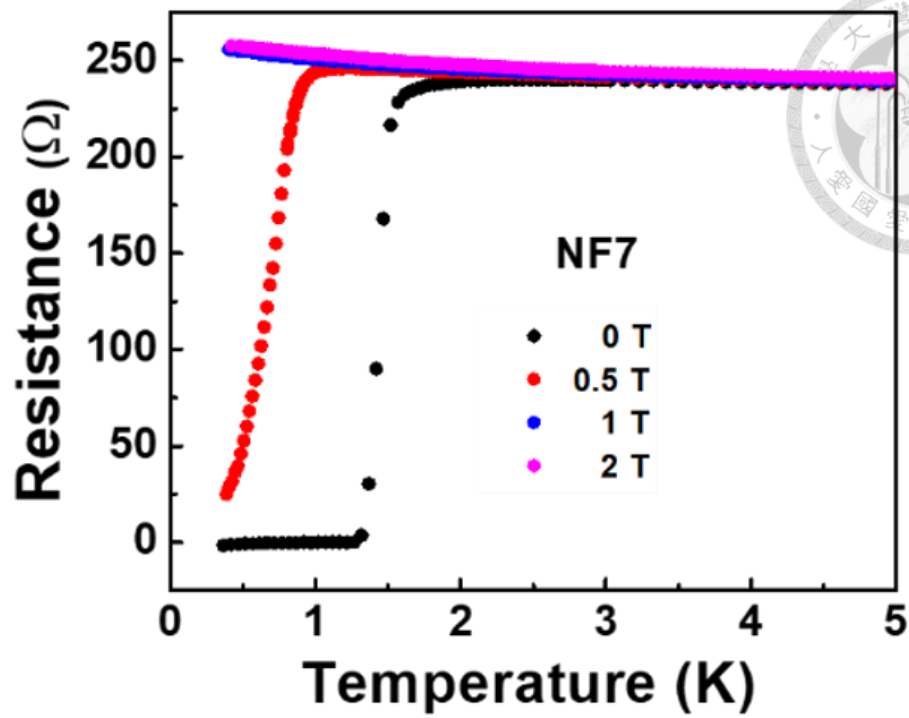


Fig.II.4. 9 The NF7 temperature dependent transport properties at various perpendicular magnetic fields.

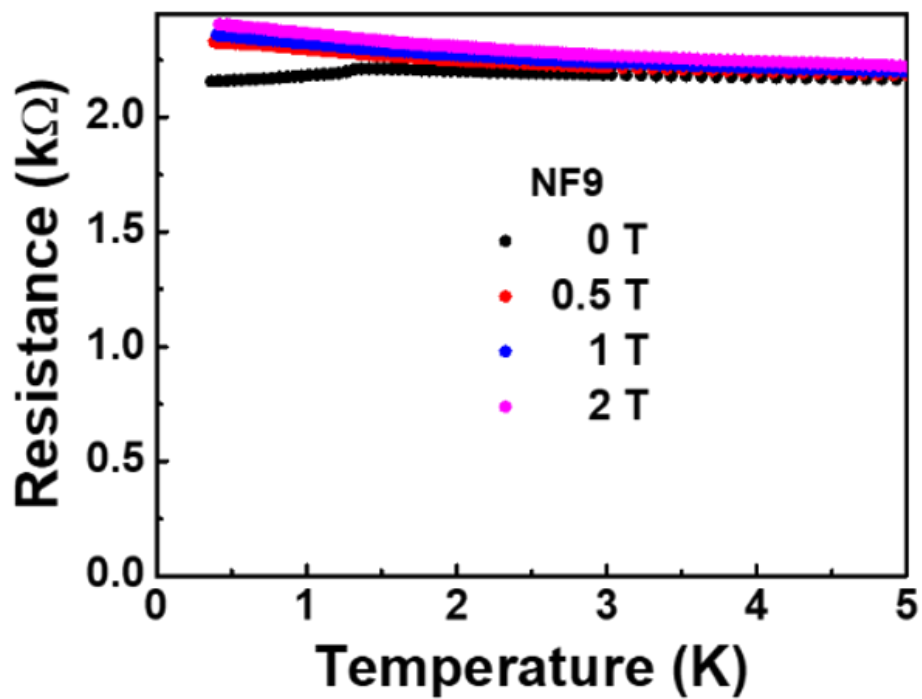


Fig.II.4. 10 The NF9 temperature dependent transport properties at various perpendicular magnetic fields.

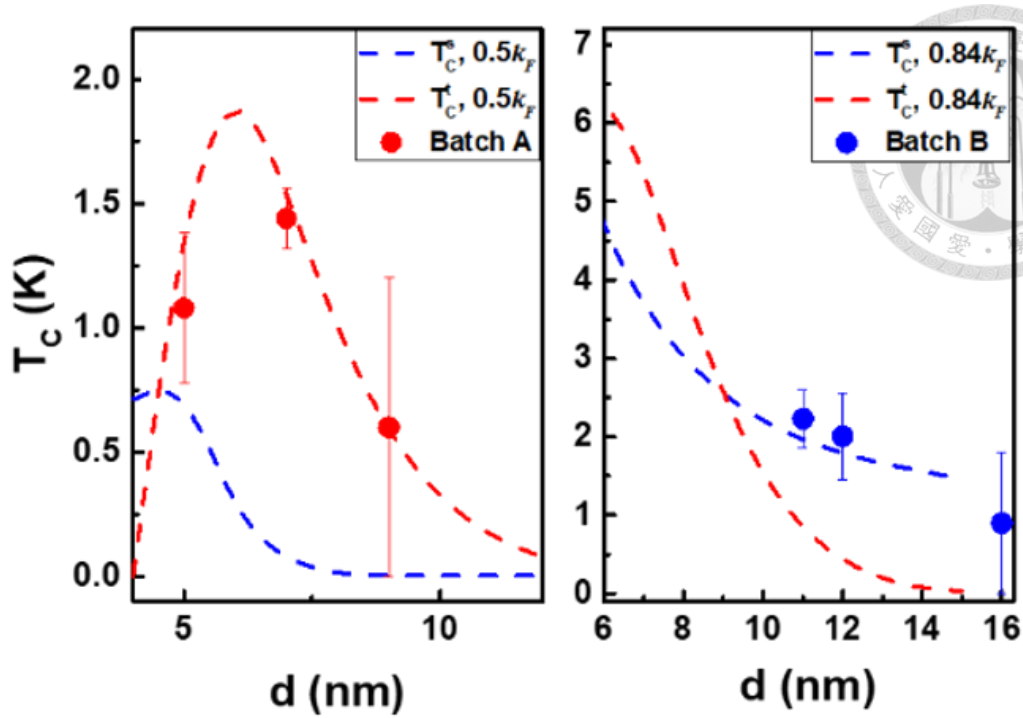


Fig.II.4. 11 The thickness dependent superconducting transition temperature T_C at zero fields.

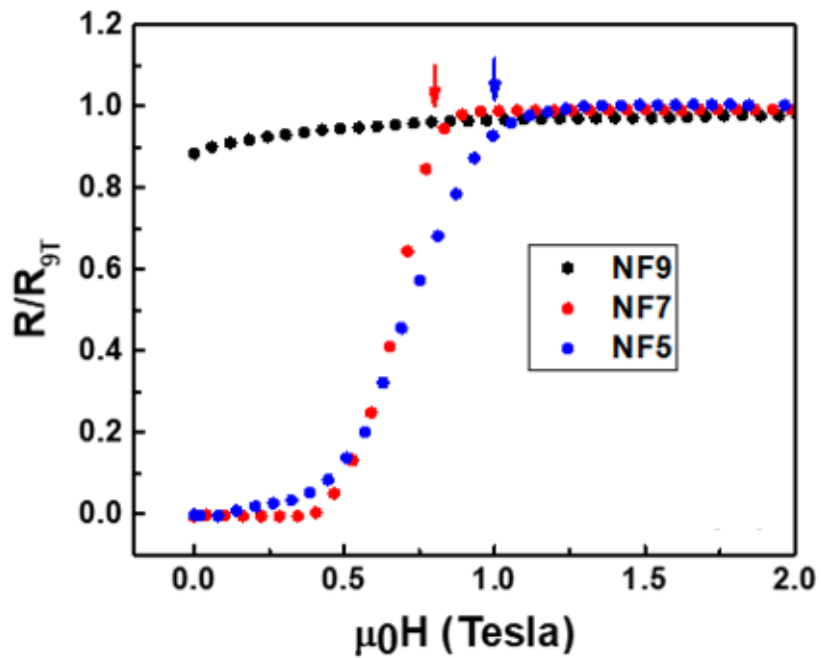


Fig.II.4. 12 Normalized perpendicular magnetic field dependent resistivity of NF5, NF7 and NF9 at 0.3K, where they are normalized by the resistivity of normal state at

9 Tesla of each samples. The upper critical fields are determined by the onset of decreasing resistivity as indicated by arrows (H_{C2}).

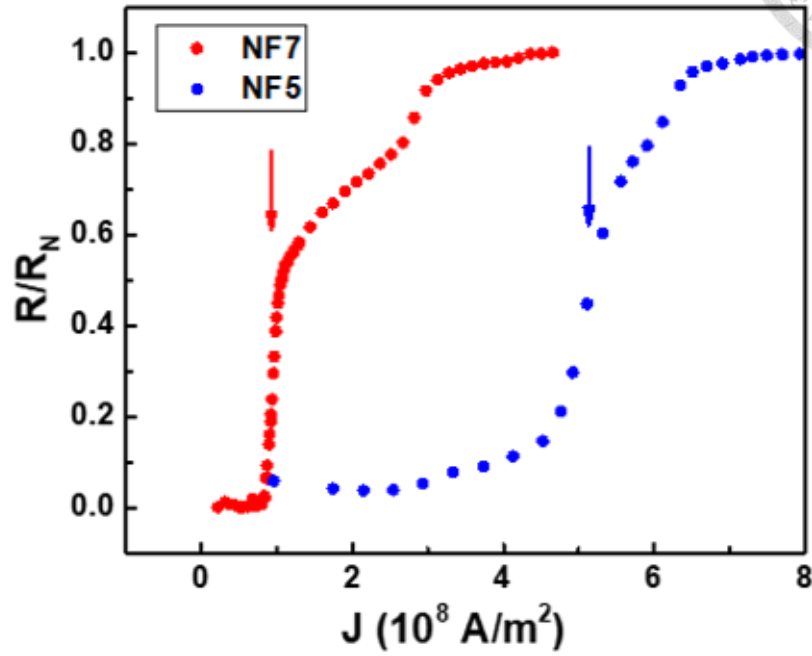


Fig.II.4. 13 The normalized current dependent resistivity of NF5 and NF7, where they are normalized by the resistivity of normal state (R_N), arrows point out the corresponding critical current density (J_C).

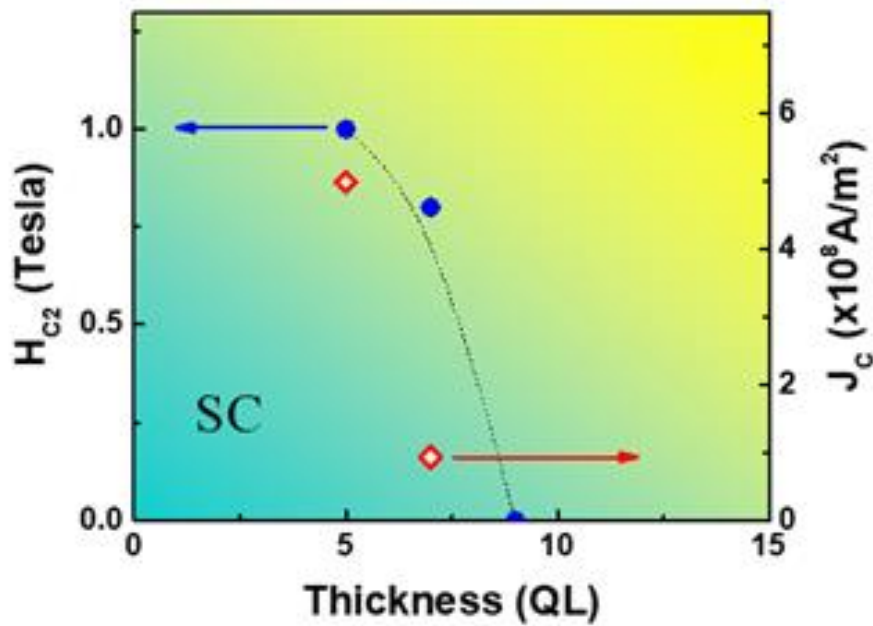


Fig.II.4. 14 The thickness dependent H_{C2} and J_C .

4.6 Theoretical analysis and mechanism of superconductivity



The superconductivity in Sb_2Te_3 nanoflakes can happen through two different pairing channels as illustrated in Fig.II.4.15 [75]. Here the pairing amplitude in the same surface Dirac cone is represented by Δ_s while the pairing amplitude between top and bottom surface Dirac cones is represented by Δ_t . The inter-surface pairing Δ_t is a purely triplet-pairing but the intra-surface pairing Δ_s is an equal mixture of singlet and triplet pairing. Both pairing channels contribute the energy of quasi-particles in the form $E_k = \sqrt{\xi_k^2 + \Delta_s^2 + \Delta_t^2}$ with ξ_k being the energy dispersion that includes the hybridization of top and bottom surface states. The pairing strength and the superconducting transition can be analyzed by including both the attractive interaction due to phonons and the Coulomb repulsive interaction. Generally, Δ_s and Δ_t satisfy gap equations governed by the net attractive potential $V_\alpha(k, p)$ ($\alpha = s$ or t) and E_k

$$\Delta_\alpha = - \sum_p V_\alpha(k, p) \frac{\tanh(\frac{\beta E_p}{2})}{2E_p} \Delta_\alpha \quad (4)$$

where $\beta = 1/k_B T$ is the inverse of temperature. Since the net potential $V_\alpha(k, p)$ is different for different pairing channel, the gap equation can not be satisfied for both Δ_s and Δ_t at the same time. Hence the intra-surface pairing Δ_s and the inter-surface pairing Δ_t can not coexist and only one of the pairing amplitudes can appear for a given thickness d . The pairing symmetry for a given thickness can be thus found only

by explicitly computing the transition temperature of Eq. (4).

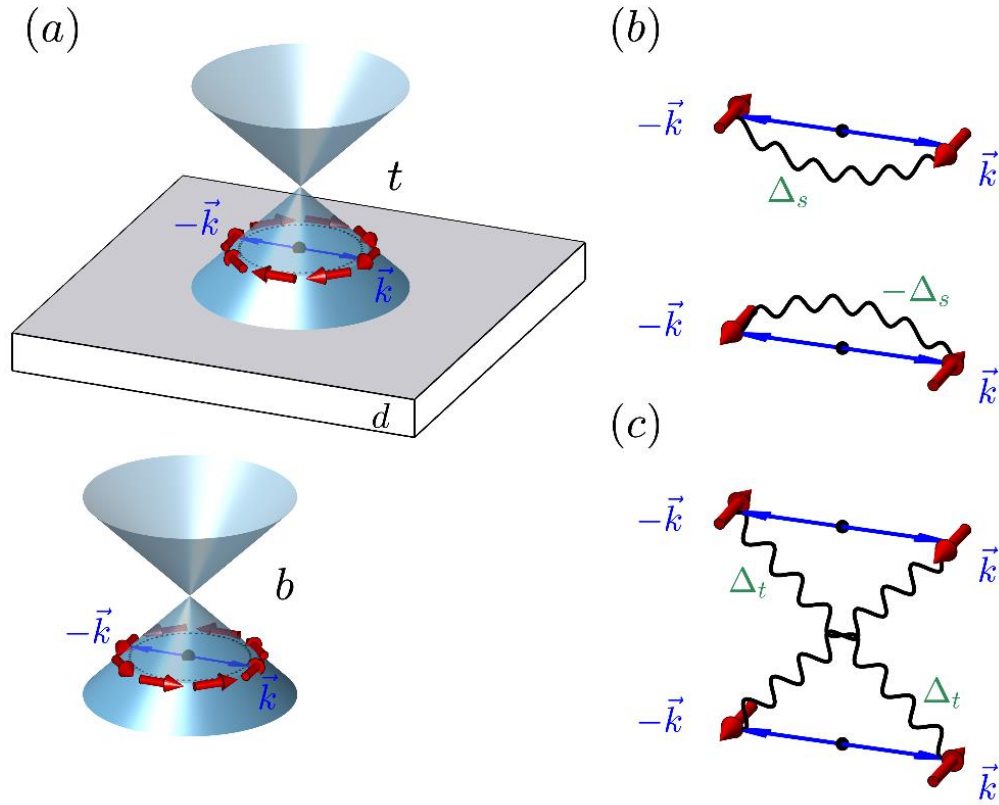


Fig.II.4. 15 A schematic plot of Dirac cones for the top (t) and bottom (b) surfaces of a nanoflake with thickness d , showing intra-surface pairing—the pairing of electrons on the same surface [75].

In the general situation when the electron-phonon coupling is not weak, the transition temperature can be best described by McMillan formula

$$T_c = \frac{\theta_D}{1.45} \exp \left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+1.62\lambda)} \right] \quad (5)$$

The Debye temperature, θ_D , represents the temperature associated with lattice vibrations, while λ is the electron-phonon coupling constant. The Coulomb

pseudopotential, μ^* , is expressed as $\mu^* = \mu/[1 + \ln (\Lambda/\omega_c)]$, where μ denotes the Coulomb interaction strength, Λ is on the order of the plasma frequency, and ω_c is the cutoff energy for electrons near the Fermi level. For Sb₂Te₃ nanoflakes, the Debye temperature is approximately 180 K. We set $\omega_c = \theta_D$ and define Λ as the distance from the Dirac point to the Fermi energy. The speed of phonons is $v_p = 2$ km/s. and the decay length ξ_d is around 1.2 nm. The mass of ions is taken as 124.7 u, and the ion charge is assumed to be the average of 3e and 4e, which is 3.53e.

By further including the screening effect, the Coulomb interaction strength depends on both the Fermi energy and sample thickness. In Fig.II.4.16, we show the computed thickness dependence of electron-phonon coupling λ , strength of Coulomb interaction μ , and transition temperatures T_c for three different Fermi wavelengths, representing Batch A samples, Batch B samples, and the bulk Sb₂Te₃. Note that for a given thickness, the pairing symmetry of the nanoflake is determined by the pairing channel with highest T_c . Due to the finite thickness, the inter-surface Coulomb interaction strength is always weaker than the intra-surface Coulomb interaction. Therefore, in large thickness limit, the intra-surface Coulomb interaction always dominates. In this limit, the superconductivity results from the competition between intra-surface Coulomb interaction and electron-phonon coupling. For large Fermi energies as shown in Fig.II.4.16c, the Coulomb interaction is screened strongly. Hence

the resulting intra-surface superconductivity survives in bulk Sb₂Te₃. For small Fermi energies as shown in Fig.II.4.16a and Fig.II.4.16b [75]., however, the screening of the Coulomb interaction is weaker. The intra-surface superconductivity approaches to vanish in the bulk limit.

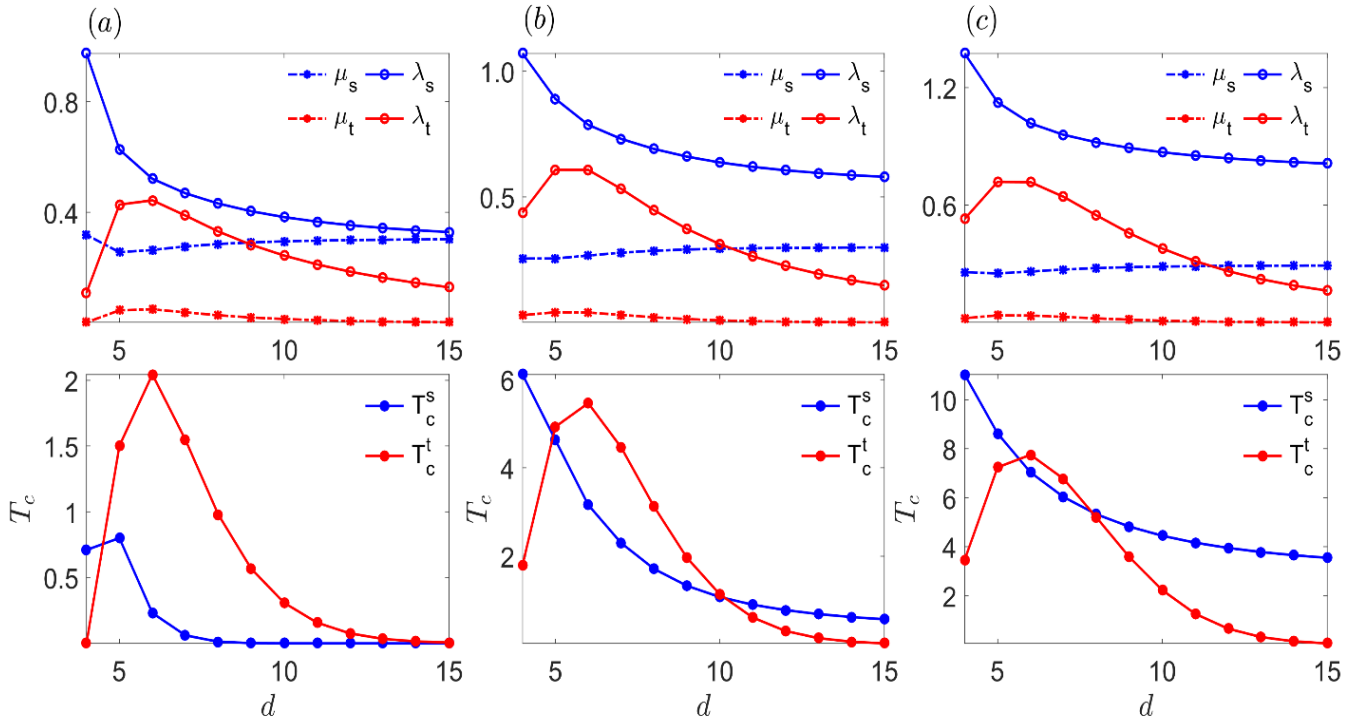
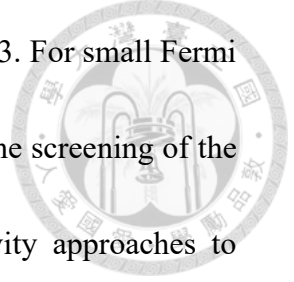


Fig.II.4. 16 The electron-phonon coupling λ , thickness dependence, the Coulomb interaction strength μ , and the transition temperatures T_c for three distinct Fermi wavelengths that simulate Batch A, Batch B, and bulk Sb₂Te₃ are as follows:: (a) Samples from Batch A are $0.5k_F$ (b) Samples from Batch B are $0.84k_F$ (c) k_F corresponds to the bulk Sb₂Te₃ Fermi wavelength. In this context, d represents the number of quintuple layers. The intra-surface and inter-surface quantities are denoted

by the subscripts s and t , respectively. The Debye temperature is set to 180 K, the phonon speed is set to $v_p = 2$ km/s, the decay length is set to $\xi_d = 1.2$ nm, the ion mass is set to 124.7 u, and the ion charge is assumed to be the average of $3e$ and $4e$, or $3.53e$ [75].

For small thickness sample, the inter-surface electron-phonon coupling becomes important. The competition between intra-surface pairing and inter-surface pairing is thus driven by the competition between intra-surface and inter-surface electron-phonon couplings. It is seen that for bulk Sb_2Te_3 , the pairing is predominantly the intra-surface pairing in each individual surface except for a couple of sample thickness in which the inter-surface pairing wins over. For Sb_2Te_3 nanoflakes between 5QLs and 9 QLs, the inter-surface pairing starts to dominate for both Batch A and Batch B samples, while the intra-surface pairing dominates over again when the hybridization gap is fully formed below 5 QLs. For samples with thickness below 4 QLs, without further doping, the Fermi energy would lie inside the hybridization gap. As a result, superconductivity disappears below 4 QLs.

Therefore, we conclude that for samples with smaller Fermi energies such as Batch A and Batch B samples, the pairing symmetry is unambiguously dominated by the triple pairing Δ_t . The exact pairing symmetry is determined by re-expressing the attractive

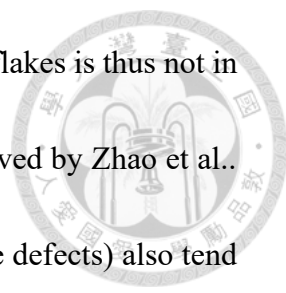
potential $V_t(\mathbf{k}, \mathbf{p})$ in terms of the energy eigenstates. This is similar to the Fu and Kane's proposal of generating topological superconductivity through the proximity of the surface Dirac cone states to a s-wave superconductor. By combining the surface Dirac cone states and $V_t(\mathbf{k}, \mathbf{p})$, we find that Δ_t leads to spinful $p_x + ip_y$ pairing. Hence Batch A samples are dominated by the triplet $p_x + ip_y$ pairing [75], which is in agreement with the measurements of in-plane upper critical fields.

Chapter 5 Conclusion

Although the aforementioned depiction of topological superconductivity pertains to Sb_2Te_3 nanoflakes cultivated in our investigations, we anticipate that the same technique can be extended to other surface states of three-dimensional topological insulators. In conventional superconductivity in bulk materials, singlet and triplet pairing channels are projected into distinct channels but are governed by the same electron-electron and electron-phonon interactions. As a result, the condition for odd-parity superconductivity is usually difficult to be satisfied in bulk materials, and this results in the rareness of natural topological superconductors. The occurrence of the inter-surface pairing presented in this work illuminates a new path to topological superconductivity. It is the separation of surface Dirac cone states in 3D topological insulators that makes it possible to split the behavior of the triplet pairing and the singlet

pairing channels for materials in thin film geometry. The difference in electron-electron interactions and electron-phonon interactions for electrons in intra-surface states and inter-surface states allows the odd-parity superconducting channel to dominate through the change of sample thickness.

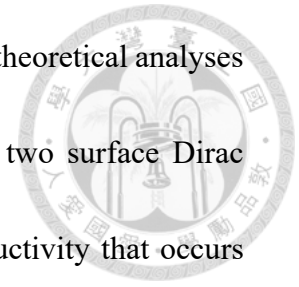
Experimentally, in addition to the control of sample thickness, the occurrence of superconductivity also relies on the ability to tune the electron density through the control of the Fermi energy. For Sb_2Te_3 crystals, the sample is extreme sensitive to the growth parameters as also noticed by Zhao et al. [59]. In fact, as revealed in the STM measurements, surfaces of bulk Sb_2Te_3 crystals exhibit large charge fluctuations as patches of superconducting regions with different superconducting gaps. These superconducting puddles origin from local shifts of the Fermi energy due to bulk charge defects (or dopants) [77]. Similar charge carrier puddles are also observed in other 2D Dirac systems [78], reflecting sensitivities of surface states on bulk doping inhomogeneity as the average Fermi energy approaches the Dirac point. As a result of inhomogeneous carrier fluctuations, the electrical resistivity of bulk Sb_2Te_3 is very sensitive to the growth conditions of the Te atmosphere as shown in our work). However, for thin topological insulators, since the ratio of surface to bulk volume increases as the thickness d decreases, the charge carrier fluctuations also decrease for small thickness. As a result, one expects that superconducting states observed in Sb_2Te_3 nanoflakes are



more homogeneous. The superconducting transition in Sb_2Te_3 nanoflakes is thus not in the same class driven by percolation of superconducting gaps observed by Zhao et al.. However, for p-type Sb_2Te_3 crystals, the main bulk defects (anti-site defects) also tend to increase the hole doping. This would decrease the shift of the Fermi energy for surface states due to bulk charge defects. As a result, averagely speaking, the Fermi surface is smaller for small thickness. This explains why the Fermi surface of Batch A samples is smaller than that of Batch B samples. The fine-tuned doping control in Sb_2Te_3 nanoflakes is thus achieved through careful control of the Te vapor and p-type nature of bulk defects. While we expect that the same mechanism for inter-surface pairing can be also applied to other surface states of 3D topological insulators, the main challenge to realize the topological superconductivity through the inter-surface pairing in other systems is the fine tuning of the doping level for surface states.

In conclusion, we have illuminated a new path to topological superconductivity through the formation of inter-surface pairing for surface electrons in Sb_2Te_3 nanoflakes. When the thickness of nanoflakes is above 11QLs, we find that the superconductivity in nanoflakes is in the same class of superconductivity that occurs at individual surface of the bulk Sb_2Te_3 discovered by Zhao et al. [59]. On the other hand, for the thickness being below 11 QLs, a new class of superconductivity is found to start forming at 9 QLs and reaching maximum around 6 QLs when the surface Dirac cones at top and

bottom surfaces start to hybridize [62]. Both experimental data and theoretical analyses indicate that the superconductivity originates from pairing between two surface Dirac fermions in nanoflakes, in contrast to the intra-surface superconductivity that occurs above 11 QLs. Our results indicate that the pairing symmetry due to the coupling of inter-surface Dirac cones is unambiguously dominated by the spinful $p_x + ip_y$ pairing and forms a new class of topological superconductors [75-77].

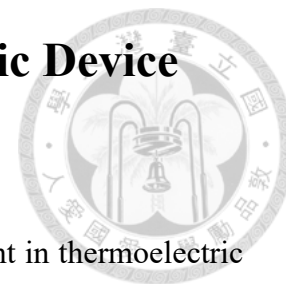




Supplementary Information:
Thermoelectric Measurement Technique
Instrumentation for Thermoelectric Performance of
Single Leg AgSbTe₂.

Chapter 1 Introduction of Thermoelectric Device

1.1 Single-Leg Thermoelectric Device



A single-leg thermoelectric device is a fundamental component in thermoelectric applications, used for power generation and cooling. It consists of a single thermoelectric material that converts temperature differences into electrical energy or vice versa using the Seebeck effect and the Peltier effect. The Seebeck effect occurs when a temperature gradient exists across the thermoelectric material, generating a voltage, which can be used for power generation. The Peltier effect occurs when an electric current flow through the thermoelectric material, creating a temperature difference, which can be used for cooling or heating applications. The core of a single-leg thermoelectric device is the thermoelectric material, which can be an n-type or p-type semiconductor.

In terms of applications, thermoelectric devices can be used for waste heat recovery in industrial processes and automotive engines, providing power to small electronic devices in environments where traditional power sources are not feasible. In cooling applications, these devices can be used for cooling electronic equipment such as CPUs and GPUs, as well as in portable coolers and refrigeration systems. In summary, a thermoelectric device is a simple yet versatile component that utilizes thermoelectric effects for power generation and thermal management. Its solid-state nature, reliability,

and scalability make it an ideal solution for various applications.



1.2 Basic Concepts of Thermoelectric Conversion Efficiency

The thermoelectric conversion efficiency (η) of a thermoelectric generator is the ratio of electrical power output to the heat power input. It is given by:

$$\eta = \frac{P_{out}}{Q_h} \times 100\% = \frac{P_{out}}{P + Q_c} \times 100\% \quad (1)$$

where P_{out} is the electrical power output and Q_h is the hot side heat, Q_c is the cold side heat. And $P_{out} = V \times I$. For an ideal thermoelectric device, the efficiency can also be expressed in terms of ZT :

$$\eta = \frac{(\Delta T)}{T_{hot}} \frac{\sqrt{1 + ZT_{avg}} - 1}{\sqrt{1 + ZT_{avg}} + \frac{T_{cold}}{T_{hot}}} \quad (2)$$

where ΔT is the temperature difference between the hot and cold sides, T_{hot} and T_{cold} are the absolute temperatures of the hot and cold sides, and ZT_{avg} is the average figure of merit of the material over the temperature range.

Chapter 2 Sample Preparation and Single-Leg Thermoelectric Efficiency Setup



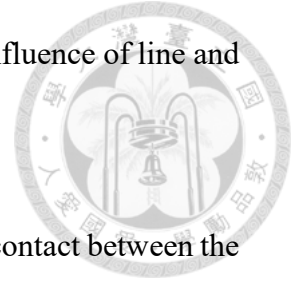
2.1 Sample Preparation

The AgSbTe_2 was synthesized using high-purity Ag shots (99.99%), Sb shots (99.999%), and Te ingots (99.999%), which were loaded into carbon-coated quartz tubes. The quartz tubes were sealed under a vacuum of approximately 4×10^{-6} Torr. The samples were slowly heated to 723 K over 8 hours, held at that temperature for 10 hours, then heated to 1148 K over 10 hours, and soaked at that temperature for 10 hours. The samples were then cooled to 698 K and annealed at this temperature for 20 hours.

2.2 Single-Leg Thermoelectric Efficiency Setup

Thermoelectric generators (TEGs) devices are designed to convert thermal energy into electrical power directly. So, the optimization of heat-to-electricity conversion efficiency stands as a paramount objective. In this work, we have employed a four-point probe methodology to quantify and compute power generation and device efficiency. A heater was strategically positioned above the apparatus, while three thermocouples were placed at distinct locations to monitor temperature fluctuations meticulously. Furthermore, the four-point probe configuration integrated a voltmeter and current

supply, strategically designed to effectively alleviate the potential influence of line and contact resistance during the measurement procedures [78].



We used silver paste to reduce thermal resistance and improve contact between the copper plates and the heater. Copper block (length of 11.2mm and cross-sectional area of $2.9 \times 2.9 \text{ mm}^2$) were employed as heat flux (III.3) meters to measure the heat flow through the TE leg, equipped with three K-type thermocouples embedded to determine the temperature differences (TC h: hot side; TC c: cold side; TC base: heat sink).

$$Q_{in} = \kappa \frac{A}{L} \Delta T \quad (3)$$

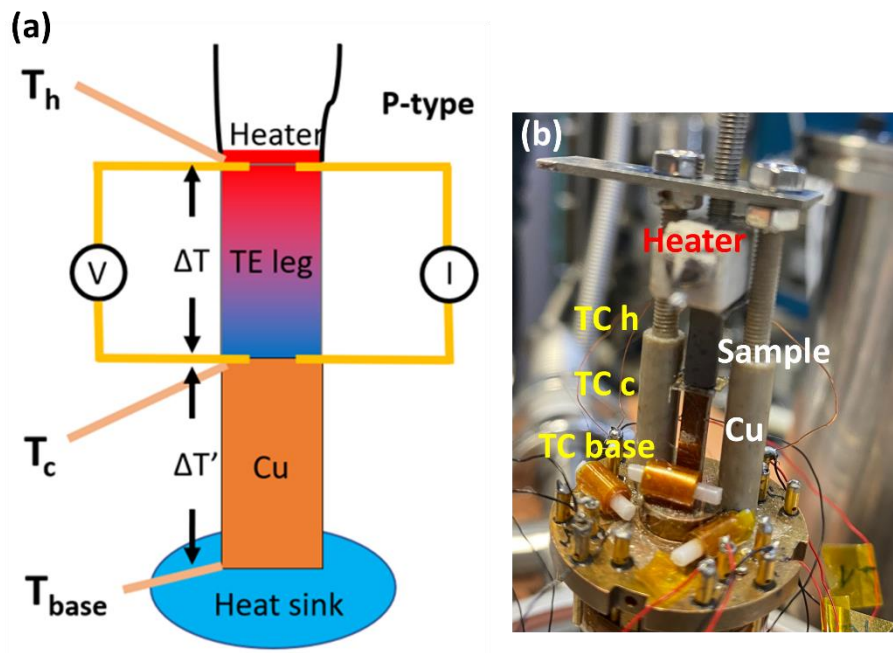


Fig.III.2. 1 Schematic diagram of the device setup. (b) Photograph of the device.

Chapter 3 Introduction of AgSbTe₂ Materials



Silver antimony telluride (AgSbTe₂) is a ternary compound that has garnered significant attention for its excellent thermoelectric properties. This material is part of a broader family of chalcogenides, which are compounds containing at least one chalcogen element (such as sulfur, selenium, or tellurium) and often exhibit interesting electronic and thermal properties. AgSbTe₂ crystallizes in a cubic or rhombohedral crystal structure, depending on the specific synthesis conditions. The structure is characterized by a complex arrangement of Ag, Sb, and Te atoms, which contributes to its unique electronic and thermal properties. The crystal lattice typically consists of alternating layers of silver and antimony atoms bonded with tellurium atoms, forming a three-dimensional network. Its properties include a high Seebeck coefficient, low thermal conductivity, and good electrical conductivity, making it highly effective in maintaining temperature gradients and achieving efficient thermoelectric performance.

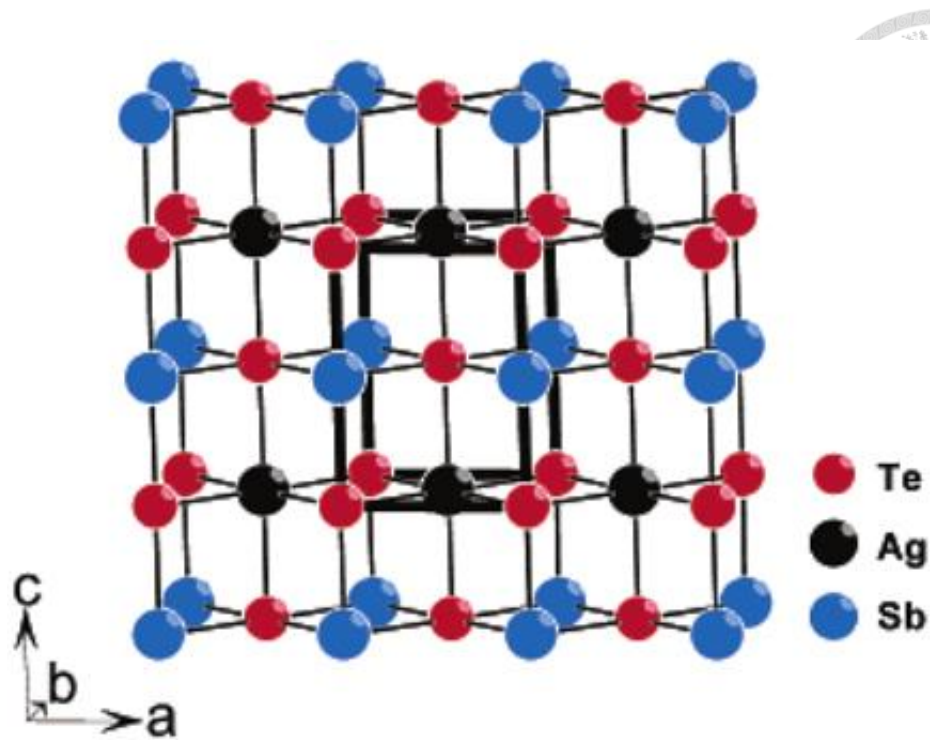


Fig.III.3. 1 AgSbTe₂ crystal structures

Chapter 4 Measurement and Characterization

4.1 Measurement of Thermal Properties

The temperatures of TC_h , TC_c , and TC_{base} can be determined using three K-type thermocouples. Additionally, the voltage difference generated by the temperature gradient can be measured using a voltmeter, allowing for the calculation of the Seebeck coefficient, which is 198 $\mu\text{V/K}$.

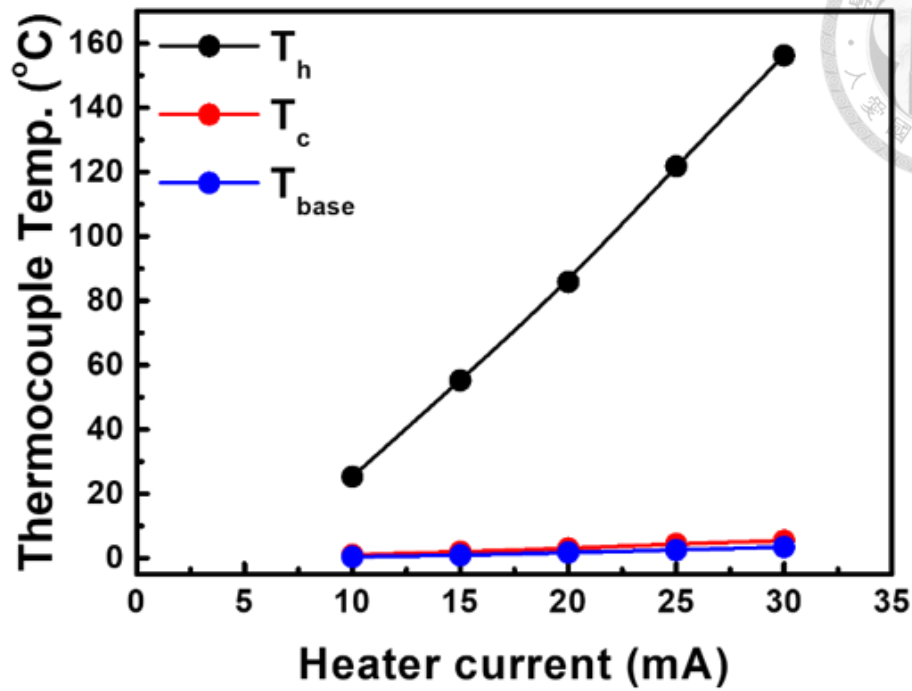


Fig.III.4. 1 Relationship between current and temperature during heater activation.

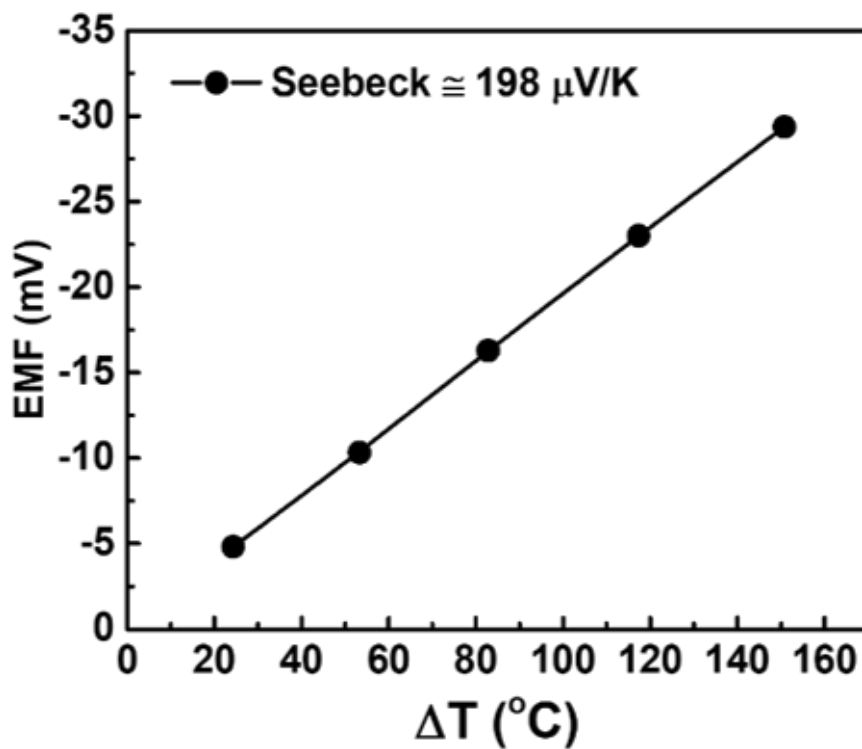


Fig.III.4. 2 The EMF during heater activation

4.2 Characterization

4.2.1 Output Power

Here, I represent the current in the circuit, V_L denotes the load voltage, V_{OC} stands for open-circuit voltage, and R signifies the internal resistance. While the current supplied by the external instrument can be accurately determined, the internal resistance, including the electrical contact resistance between the TE leg and the electrodes, significantly impacts the determination of the actual output power of the TE material.

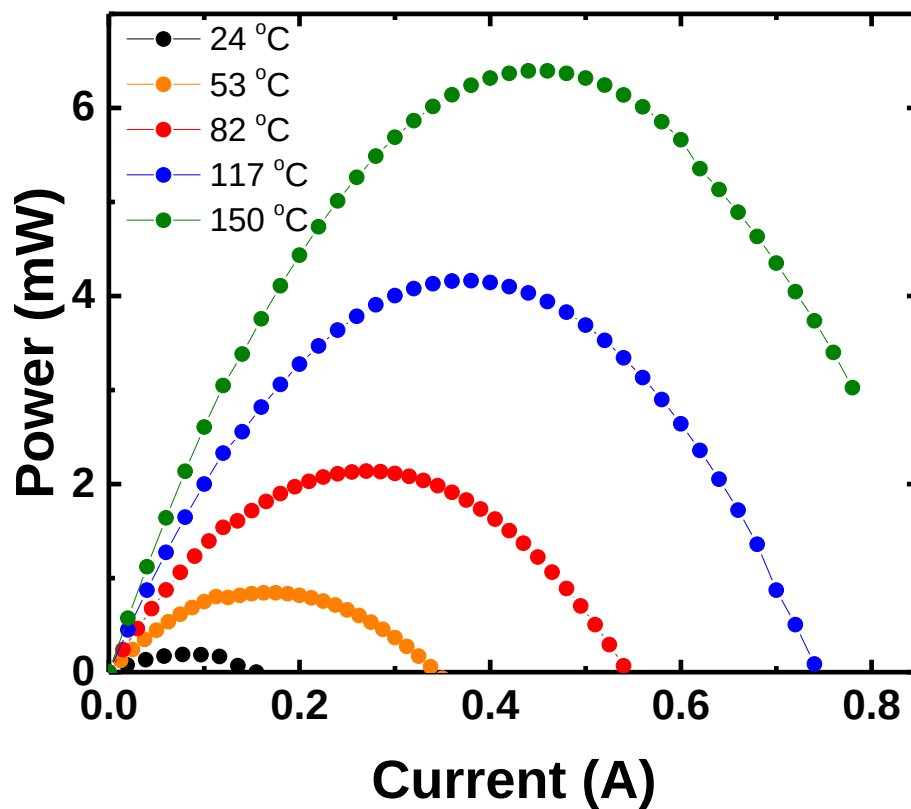


Fig.III.4. 3 Output power dependent on current



4.2.2 Single-Leg Thermoelectric Properties

The first one calculates heat input by considering the thermal conductivity, cross-sectional area, length, and temperature difference of the material, which in this case is a copper block. The second formula, on the other hand, measures the efficiency of a system. It does so by dividing the output power by the sum of the output power and the heat flow out of the cold side, expressed as a percentage. This efficiency calculation provides insight into how effectively the system converts input energy into useful output power.

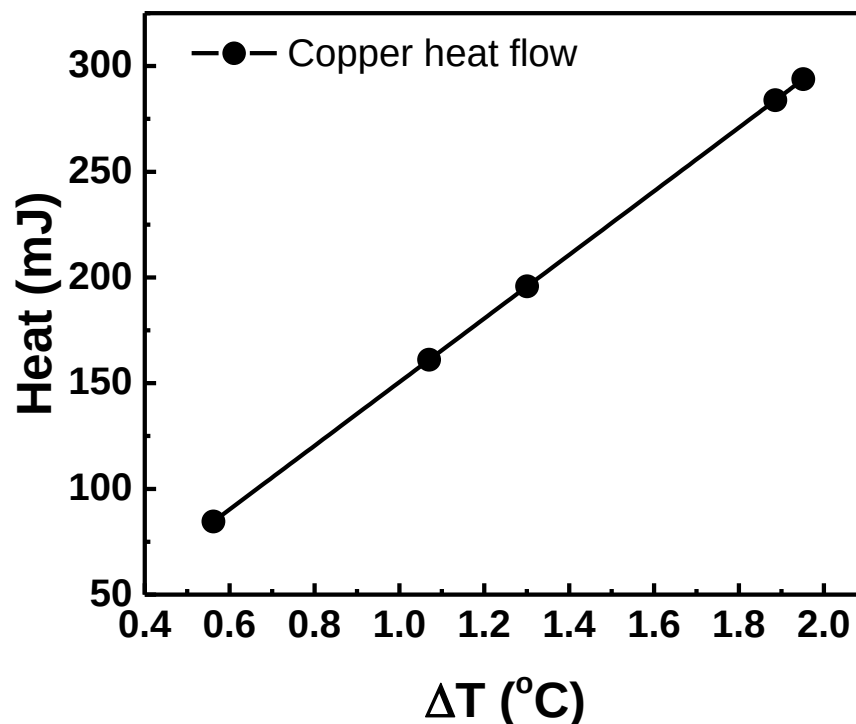


Fig.III.4. 4 The relationship between temperature gradient and heat flow in the copper block during heating.

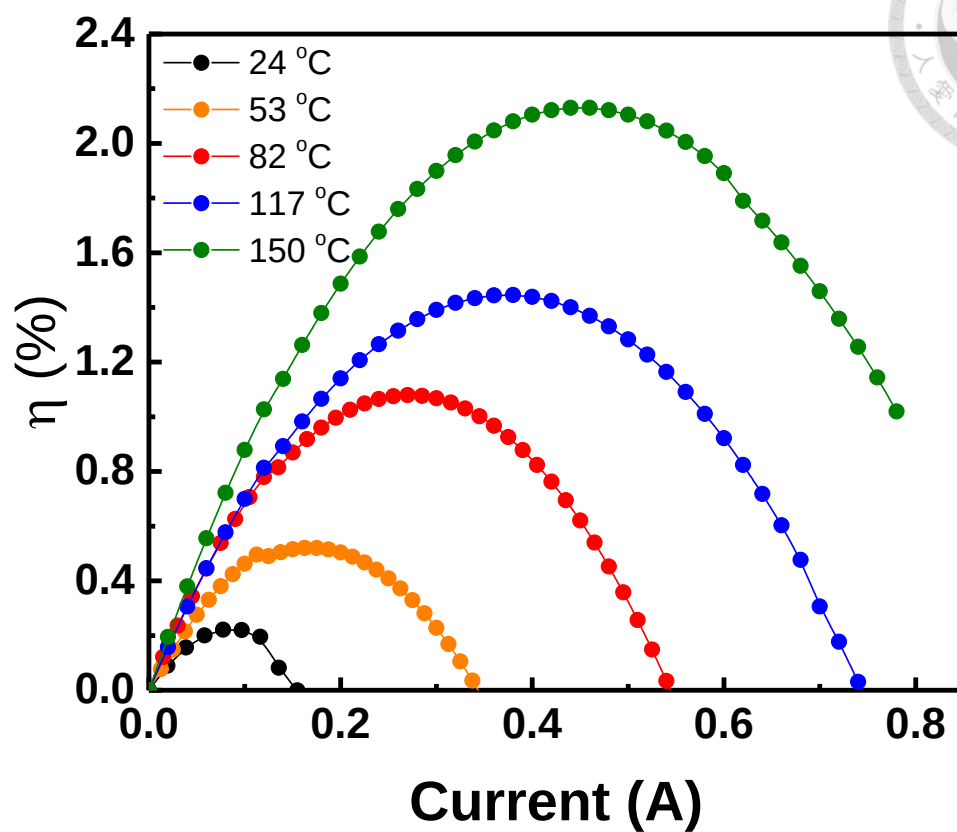
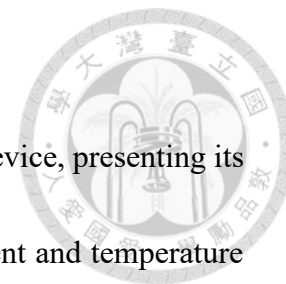


Fig.III.4. 5 The relationship between current and thermoelectric efficiency

Chapter 5 Conclusion

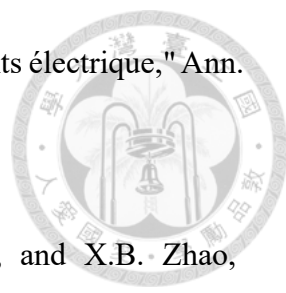


In summary, our study focused on a Single-Leg Thermoelectric Device, presenting its setup and components. We explored the relationship between current and temperature during heater activation, observing a maximum temperature difference of 150°C as the current varied from 10mA to 30mA. Additionally, by analyzing temperature gradients and EMF, we determined the Seebeck coefficient as $198\ \mu\text{V/K}$. Furthermore, varying the current from 0A to 0.8A, resulted in a peak power output of 6.4mW. Lastly, we examined the correlation between current and thermoelectric efficiency, achieving a maximum value of 2.1% at a temperature difference of 150 degrees Celsius. The efficiency obtained at the same temperature difference is similar to that of the reference literature [79,80]. These findings provide valuable insights into thermoelectric device behavior and potential optimization for enhanced energy conversion.

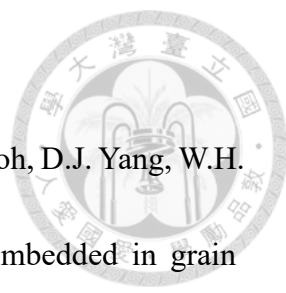
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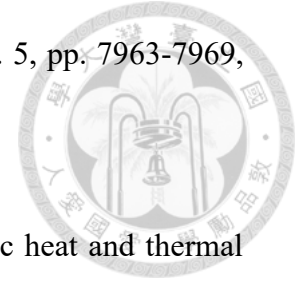
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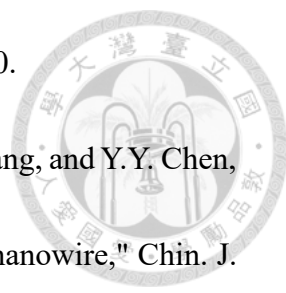
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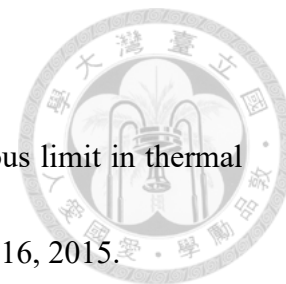


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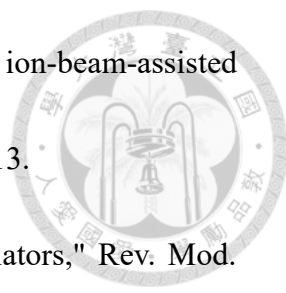
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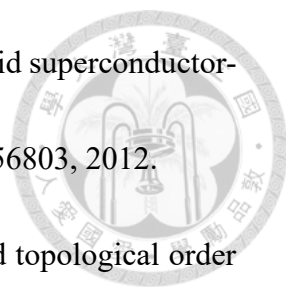
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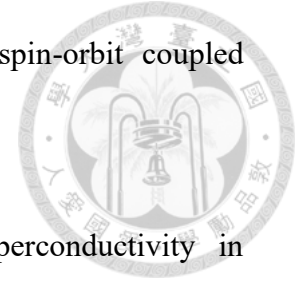


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