



Thermal and thermoelectric transport properties in single MXene flakes

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Abstract

MXenes are being increasingly explored for electronics at the micro- and nanoscale. In recent years, their electrical, optical, mechanical, and electrochemical properties of single flakes have been gradually investigated. However, thermal and thermoelectric transport at the single-flake level remains largely unexplored. A fundamental understanding of local thermal and thermoelectric processes can inform the design of novel micro- and nano-devices and enhance their efficiency. In this thesis, the nanoscale thermal and thermoelectric transport properties of several types of MXenes, primarily $\text{Ti}_3\text{C}_2\text{T}_x$, are studied using the scanning thermal microscopy (SThM) technique. This method allows to quantitatively measure the local thermal resistance and thermovoltage maps with a thermoresistive probe. First, thickness-dependent thermal transport from monolayer to few-layer MXene flakes is investigated. A diffusive thermal transport model is employed to extract the thermal conductivity and the thermal interface resistivity. An ultra-low thermal conductivity of $0.78 \text{ W m}^{-1} \text{ K}^{-1}$ in $\text{Ti}_3\text{C}_2\text{T}_x$ MXene is observed, which is much lower than the value predicted by the Wiedemann–Franz (WF) law. The results reveal the underlying transport behavior and suggest the presence of strong electron–phonon interactions. Second, the layer-dependent thermoelectric properties are studied by stacking single-layer $\text{Ti}_3\text{C}_2\text{T}_x$ layer-by-layer on the pre-patterned micro-bridge device. The interlayer interaction can lead to a change in the band structure and in turn result in a Seebeck coefficient

change across the homostructures. Last, local thermoelectric mapping in MXene homostructures is performed using SThM in both AC (2ω method) and DC modes. The thermovoltage response along the junction is observed, and the corresponding Seebeck coefficient variation map is reconstructed using a deconvolution method. The high resolution thermovoltage maps demonstrate the influence of layer thickness, metallic contacts, local defects and surface terminations on the local Seebeck coefficient in MXene. This work aims to improve our understanding of local transport properties in single MXene flakes and to open new paths for designing high-performance devices with broader applications.

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Scientific publications

1. *Violation of the Wiedemann–Franz Law and Ultralow Thermal Conductivity of $Ti_3C_2T_x$ MXene*. **Yubin Huang**, Jean Spiece, Tetiana Parker, Asaph Lee, Yury Gogotsi and Pascal Gehring*. ACS Nano, 18 (47), 32491–32497, 2024.
2. *Roadmap on printable electronic materials for next-generation sensors*. Vincenzo Pecunia*, Luisa Petti*, Joseph B Andrews*, ..., **Yubin Hunag**, Jean Spiece, Pascal Gehring and et al. Nano Futures, 8, 032001, 2024.
3. *Single-material MoS_2 thermoelectric junction enabled by substrate engineering*. Mohammadali Razeghi, Jean Spiece, Oğuzhan Oğuz, Doruk Pehlivanoglu, **Yubin Huang**, Ali Sheraz, Uğur Başçı, Phillip S Dobson, Jonathan MR Weaver, Pascal Gehring, Kasırga, T. Serkan. npj 2D Materials and Applications, 7 (1), 36, 2023.

Glossary

α	Temperature coefficient of resistance
ϵ	Energy
ΔS	Seebeck difference
ΔT	Temperature difference
ΔV	Voltage difference
Λ	Phonon mean free path
λ	Wavelength
κ	Thermal conductivity
κ_e	Electronic thermal conductivity
κ_{eff}	Effective thermal conductivity
κ_c	Cross-plane thermal conductivity
κ_i	In-plane thermal conductivity
κ_{ph}	Phonon thermal conductivity
κ_{tot}	Total thermal conductivity
∇T	Temperature gradient
ν	Group velocity
μ	Charge mobility
$\mu(E)$	Energy dependent charge mobility
Ω	Ohm (unit)
ω	Angular frequency
Π	Peltier coefficient
ρ	Mass density
σ	Electrical conductivity
$\sigma(E)$	Energy dependent conductivity

τ	Relaxation time
$\tau(E)$	Energy dependent relaxation time
θ	Minimum resolvable angle
A	Cross-sectional area
a	Radius
Al_2O_3	Aluminum oxide
c	Speed of sound
c_p	Specific heat capacity at constant pressure
D	Characteristic size
e	Electron charge
E_F	Fermi energy
$\mathbf{F}$	External force
f	Phonon distribution function
$f(E)$	Fermi function
G_{air}	Gas thermal conductance
G_{rad}	Radiation thermal conductance
G_p	Probe thermal conductance
G_{ss}	Solid-solid thermal conductance
G_{th}	Thermal conductance
G_w	Water meniscus thermal conductance
$g(E)$	Energy dependent density of states
H_2O	Water
HF	Hydrofluoric acid
HCl	hydrochloric acid
I	Electrical current
K_n	Knudsen number
k_B	Boltzmann constant
L	Length
L_0	Lorentz number
LiCl	Lithium chloride
LiF	Lithium fluoride
m^*	Electron effective mass
MoS_2	Molybdenum disulfide
MXenes	Transition metal carbides and/or nitrides

NH_4F	Ammonium fluoride
n	Carrier density
$n(E)$	Energy dependent carrier density
P	Power
q	Heat flow
$\mathbf{q}$	Wave vector
$\dot{Q}$	Volumetric thermal energy generation rate
R	Resistance
R_{int}	Interface thermal resistance
R_{p}	Probe thermal resistance
R_{p0}	Probe thermal resistance at a reference temperature
R_{probe}	Probe electrical resistance
R_{th}	Thermal resistance
R_{tip}	Tip thermal resistance
R_{spr}	Spreading thermal resistance
r_{int}	Interface thermal resistivity
s	Phonon polarization
S	Seebeck coefficient
S_{tot}	Total Seebeck coefficient
SiO_2	Silicon oxide
SiN_x	Silicon nitride with variable stoichiometry
Si_3N_4	Silicon nitride
T	Temperature
T_{c}	Cold temperature
T_{h}	Hot temperature
T_{m}	Microscope temperature
T_{s}	Sample temperature
t	Thickness
t_{eff}	Effective thickness
TiO_2	Titanium dioxide
V	Potential drop (voltage)
V_{c}	In-contact SThM signal
V_{nc}	Non-contact SThM signal
V_{sthm}	SThM output voltage

$\mathbf{v}$ Phonon group velocity

Z Acoustic impedance

ZT Figure of merit

Acronyms

2D	Two-dimensional
A	Ampere (unit)
AFM	Atomic force microscope
Ag	Silver (element)
Al	Aluminum (element)
AMM	Acoustic-mismatch mode
Au	Gold (element)
BP	Black phosphorus
BTE	Boltzmann transport equation
C	Coulomb (unit)
C	Carbon (element)
CCD	Charge-coupled device
CNP	Charge neutrality point
Cr	Chromium (element)
Cu	Copper (element)
CVD	Chemical vapor deposition
DFT	Density functional theory
DMF	Dimethylformamide
DMM	Diffuse mismatch mode
DMSO	Dimethylsulfoxide
DOS	Density of states
EBL	Electron beam lithography
eff	Effective
eV	Electron volt

fcc Face-centered cubic
FDTR Frequency-domain thermoreflectance
Ga Gallium (element)
g Gram (unit)
hBN Hexagonal boron nitride
IR Infrared
IPA Isopropanol
J Joule (unit)
K Kelvin (unit)
KPFM Kelvin probe force microscopy
LEED Low electron energy diffraction
LO Longitudinal optical
NEGF Non-equilibrium Green's function
m Meter (unit)
M Molar (unit)
MAA Methacrylic acid
MIBK Methyl isobutyl ketone
Mo Molybdenum (element)
MD Molecular dynamics MFP Mean free path
PCB Printed circuit board
Pd Palladium (element)
PDMS Polydimethylsiloxane
pH Potential hydrogen
PID Proportional–integral–derivative
PMMA Poly(methyl methacrylate)
PPC Poly(propylene carbonate)
Pt Platinum (element)
rpm Revolutions per minute
s Second (unit)
SEM Scanning electron microscope
Si Silicon (element)
SNOM Scanning near-field optical microscopy
SPM Scanning probe microscopy
SThEM Scanning thermoelectric microscopy

SThM Scanning thermal microscopy
STM Scanning tunnelling microscope
STP Scanning thermal profile
T Temperature
tBLG Twisted bilayer graphene
Ti Titanium (element)
TDTR Time-domain thermorefectance
TEM Transmission electron microscopy
TMAOH Tetramethylammonium hydroxide
TMDs Transition metal dichalcogenide
TO Transverse optical
TRI Thermorefectance thermal imaging
UCLouvain Université catholique de Louvain
V Vanadium (element)
V Volt (unit)
vdW van der Waals
WF Wiedemann-Franz
W Watt (unit)

Chapter 1

Introduction

1.1 Layered 2D materials and MXenes

Since the discovery of graphene in 2004, many two-dimensional (2D) layered materials have been widely explored and developed for next-generation technologies due to their outstanding and tunable optical, electrical, thermal and mechanical properties [1–3]. These atomically thin layers are primarily held together by van der Waals interactions, allowing for easy exfoliation from bulk crystals and stacking into homo- or heterostructures with tailored functionalities. These 2D layered materials include transition metal carbides and/or nitrides (MXenes), transition metal dichalcogenides (TMDs), black phosphorus (BP) or hexagonal boron nitride (hBN). Their unique properties provide a versatile platform for advanced 2D electronics and nanotechnology [2].

MXenes are an emerging family of 2D materials with a wide range of applications, including energy storage, electromagnetic interference shielding, optoelectronics, flexible electronics, and sensors [4, 5]. They are typically synthesized through selective chemical etching of MAX phases—for example from Ti_3AlC_2 (bulk MAX) to $\text{Ti}_3\text{C}_2\text{T}_x$ (2D MXene), where T_x represents the surface terminations

[6]. This unique combination of metallic conductivity and tunable surface chemistry makes them highly versatile, driving advancements in many research fields. Another important advantage of MXenes is that they can be exfoliated in liquids, which enable large-scale production (*e.g.*, MXene films or wafer-scale assembly) compared to traditional mechanical exfoliation methods.

1.1.1 Structure of MXenes

The MXene's family has expanded significantly since the first discovery of single-crystal $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in 2011, with over 40 compositions experimentally synthesized and more than a hundred theoretically predicted MXenes to date [4, 7, 8]. They are well established with the general formula $\text{M}_{n+1}\text{X}_n\text{T}_x$, where $n = 1, 2, 3$ or 4, M represents an early transition metal, X is carbon and/or nitrogen, and T_x are the surface terminations (*e.g.*, =O, -OH, -F, -Cl). For example, the most common titanium carbide MXene with three layers of transition metal ($n = 2$) and random surface terminations is denoted as $\text{Ti}_3\text{C}_2\text{T}_x$, and a fully oxygen-terminated form would be written as $\text{Ti}_3\text{C}_2\text{O}_2$. The element compositions and four type of common structures of MXenes are summarized in Figure 1.1. The rich combination of transition metal elements and the presence of mixed surface terminations make MXenes a diverse and expansive family of 2D materials. Compared to their bulk counterparts (multilayers), MXenes show a distinct 2D nature when their thickness is reduced to single or few layers. To date, a wide range of single- or few-layer MXenes (such as $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{Nb}_4\text{C}_3\text{T}_x$, Mo_2CT_x , V_2CT_x) have been experimentally synthesized and extensively studied for their mechanical, optical and transport properties.

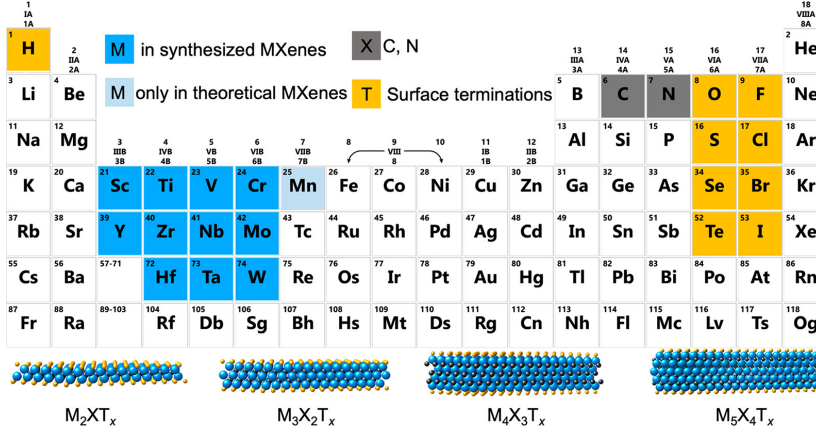


Figure 1.1: Periodic table showing compositions of MXenes. Elements used to build MXenes are marked with different colors. The schematics of four typical structures of MXenes are presented at the bottom. Figure reproduced from Ref. [5].

MXenes have a hexagonal crystal structure with a space group symmetry of $P6_3/mmc$. As an example, Figure 1.2a shows the structure model of an ideal $Ti_3C_2O_2$. Its crystal structure is confirmed by the low electron energy diffraction (LEED) image, showing a clean well-ordered hexagonal surface (Figure 1.2b). Figure 1.2c illustrates three high-symmetry points in Brillouin zones: $\Gamma(0, 0, 0)$, $M(1/2, 0, 0)$, $K(2/3, 1/3, 0)$. Two dashed high-symmetry lines along these points are highlighted and can be used for band structure calculations. Surface groups occupy different sites on the outer M layers, and their bonding depends on the types of T_x and M atoms, which together contribute to the formation of a stable structure. For the $=O$ surface species, there are two possible adsorption sites: one is a three-coordinated hollow fcc-site involving $2p - \sigma$ orbitals, and the other is a bridge site between two Ti atoms involving $2p - \pi$ orbitals (Figure 1.2a and 1.2d).

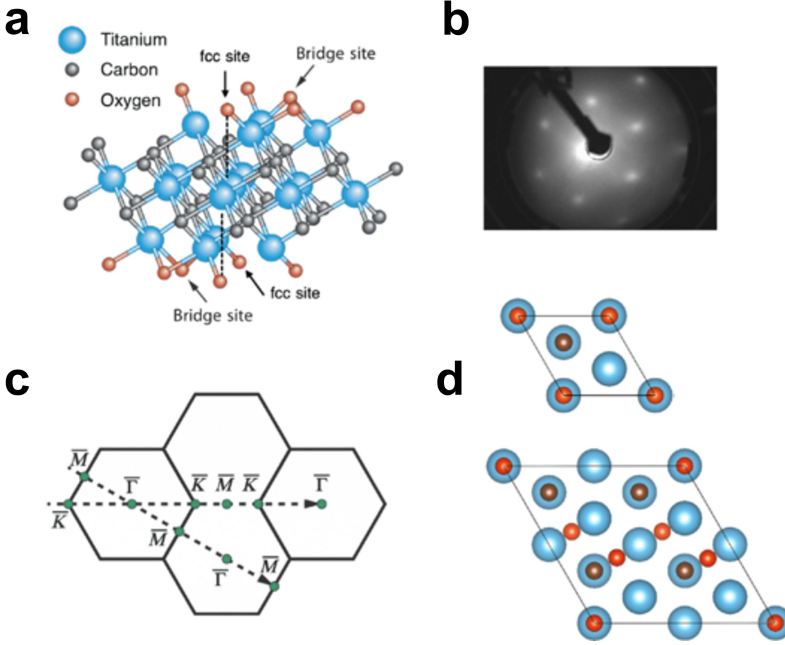


Figure 1.2: (a) Crystal structure model of $\text{Ti}_3\text{C}_2\text{O}_2$ flake by O-occupying hollow fcc and bridge sites. (b) LEED image of $\text{Ti}_3\text{C}_2\text{O}_2$ flake showing hexagonal spots. (c) Brillouin zones of the hexagonal unit cell with high-symmetry points. (d) Top views of structure models of a $\text{Ti}_3\text{C}_2\text{O}_2$ unit cell for O atom (red) on fcc and bridge sites. Figure reproduced from Ref. [9].

1.1.2 Synthesis and exfoliation of MXenes

Chemical vapor deposition (CVD) is a versatile technique for synthesizing films and 2D flakes. However, only a limited number of MXenes have been grown with CVD, such as Mo_2C , Mo_2N , TiC_x , and Ti_2CCl_2 [10]. Most of MXenes to date have been produced via wet chemical methods. Specially, MXenes can be synthesized by selective etching “A” atom from MAX phases. “A” refers to

an A-group element (mainly groups 13 to 16 of the periodic table, such as aluminium, gallium, silicon) [6, 7]. Because of the strong metal bonding in M-A atoms, direct exfoliation from MAX phase to obtain the MXene flake is difficult. Hydrofluoric acid (HF) or a combination of hydrochloric acid (HCl) and lithium fluoride (LiF) are used to etch the “A” layers. Figure 1.3a shows a common two-steps synthesis route for MXene flakes. The removal of the Al layers can dramatically weaken the bond strength between the MXene layers. The typical accordion-like MXene structure after etching from bulk MAX phase is shown in Figure 1.3c. Due to the wet chemistry synthesis method, MXene layers are terminated by surface terminations. These surface groups are directly related with the etching procedure. For example, when synthesizing MXenes in acid solutions containing fluoride ions, the surface is mainly terminated with -F and =O/-OH. Other halogens terminations such as -Cl, -Br and -I can be also achieved in Lewis-basic halides [11]. These multilayers are held together through the van der Waals force and hydrogen bonding. Both for application and for fundamental studies on their 2D nature, it is necessary to separate MXene layers into individual flakes. Previous studies have shown that multilayer MXenes exhibit much stronger interlayer interactions than graphite and TMDs [12], making it challenging to obtain thin MXene flakes through mechanical exfoliation methods such as the scotch tape technique. Liquid exfoliation methods are employed to produce large-scale single- and few-layer MXene flakes. Owing to their negative surface charge, delamination of multilayered MXenes could be achieved by further intercalating with metal cations or large organic molecules, for example, lithium ion or tetramethylammonium hydroxide (TMAOH) to increase the interlayer spacing and weaken interlayer interactions [13]. The intercalation can happen spontaneously during the etching process. Besides the ions and organic molecules, water can also intercalate between the layers in any etching process [14]. The electronic properties of MXenes can be tuned via intercalation, which depends on both the intercalant species and the interlayer spacing [15]. A

stable colloidal solution with single- or few-layer MXene flake is obtained followed by agitation or sonication. MXenes are highly hydrophilic and can be dispersed in many polar solvents, including water, ethanol, dimethylsulfoxide (DMSO), and dimethylformamide (DMF) [16]. Therefore, MXenes can be produced in various forms for applications such as films through coating or filtering, as well as inks, and powders [17]. The large-scale production of MXenes offers advantages for practical applications over many other 2D materials.

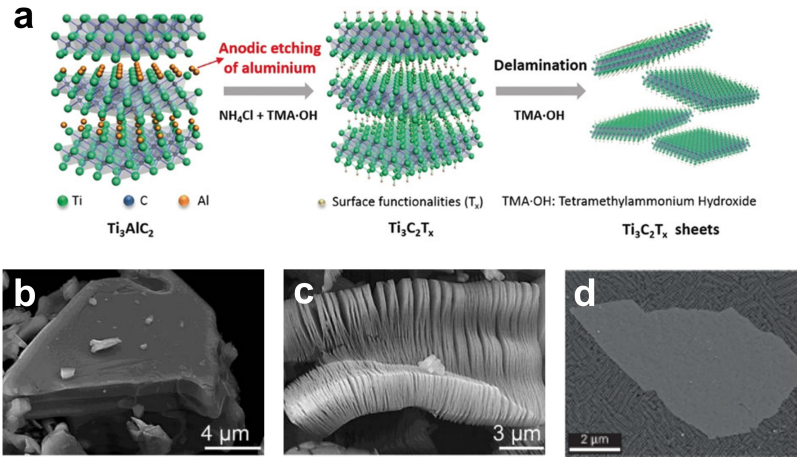


Figure 1.3: (a) Schematic of the synthesis and delamination process of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes from crystalline MAX phase. SEM images of (b) bulk Ti_3AlC_2 , (c) $\text{Ti}_3\text{C}_2\text{T}_x$ multilayer after etching process and (d) $\text{Ti}_3\text{C}_2\text{T}_x$ single flake after delamination and exfoliation. Figure reproduced from Refs. [18–20].

1.1.3 Properties and application of MXenes

In 2D layered materials, MXenes have attracted both theoretical and experimental research interest over the past ten years because of their compelling electronic, optical, mechanical and thermal properties [4, 17]. Their versatile surface chemistry and flexible compositions

endow them with unique and tunable properties, making them highly promising for many applications and research fields. With these advantages, MXenes have been studied in a wide range of fields ranging from energy storage, catalysis, optoelectronics, wearable electronics, sensors to electromagnetic interference shielding, antennas and biomedicine [4]. Recently, MXene-based micro-/nanoelectronic devices have been increasingly developing, with MXenes being used as either active layers or metal contact layers. As shown in Figure 1.4, a roadmap is proposed for the development of MXene electronic devices, including transistors, diodes, memory devices, sensors, artificial synapses, quantum computing components, and telecommunication elements. These applications require an in-depth understanding of the transport properties of MXenes.

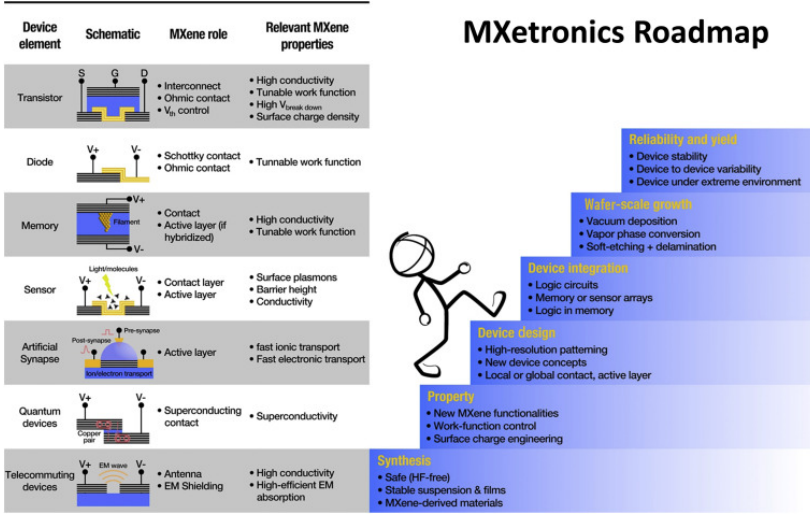


Figure 1.4: Proposed roadmap for MXene electronics. Figure reproduced from Ref. [21].

These applications are directly related to the electrical transport properties of MXenes and therefore early studies were focused on their electronic properties. Their band structure and electron density of states (DOS) have been extensively investigated using density functional theory (DFT) calculations [22]. These calculations indicate that most of them exhibit metallic to semiconducting behavior depending on the type of “M” atoms and their surface chemistry. For example, $Ti_3C_2T_x$ shows the metallic nature with a high electrical conductivity of up to $20\,000\,S\,cm^{-1}$ [23]. Recent experiments have also investigated the band structure of $Ti_3C_2O_2$ using angle-resolved photoemission spectroscopy (ARPES), clearly revealing its metallic bands at the Fermi level [9]. Some MXenes are predicted to be semiconductors, such as Mo_2CT_x [24], $Nb_4C_3T_x$ [25] and $Mo_2TiC_2T_x$ [26]. Besides, a few of MXenes with heavy “M” atoms also show unconventional electronic behaviors like topological insulators [27, 28] and superconductors (*e.g.*, Nb_2CT_x and $Ti_3C_2Br_2$ with special surface terminations [29]). However, experimental stud-

ies on their electronic properties have focused on only a few types of MXenes so far: $\text{Ti}_3\text{C}_2\text{T}_x$, Mo_2CT_x , $\text{Mo}_2\text{TiC}_2\text{T}_x$, $\text{Nb}_4\text{C}_3\text{T}_x$. This is because only a few MXenes can be synthesized as large-area single- or few-layer flakes ($>10\text{ }\mu\text{m}$). Further research requires the ability to produce high-quality, large-area thin MXene flakes.

Elastic properties of monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ MXene have been experimentally studied, and its in-plane Young's modulus is $484 \pm 13\text{ GPa}$ using nanomechanical push-to-pull devices [30], which is close to theoretically predicted value of 502 GPa [31]. The AFM nanoindentation method has also been employed to measure the elastic properties of suspended single-layer MXenes, yielding an effective Young's modulus of $330 \pm 30\text{ GPa}$ for $\text{Ti}_3\text{C}_2\text{T}_x$ [32] and $386 \pm 13\text{ GPa}$ for $\text{Nb}_4\text{C}_3\text{T}_x$ [33]. MXenes show the highest value among the solution-processable 2D materials, including graphene oxide, MoS_2 . The high mechanical properties of MXenes broaden their applications in structural composites, nanoresonators, and high-strength membranes.

Some MXenes such as Ti-based compounds show intense free carrier absorption in the near-infrared (IR) region [34]. Their excellent optical properties enable a range of advanced optical applications in plasmonics, photothermal effects, optoelectronics, ultrafast optics, nonlinear optics. In recent years, ultrafast spectroscopy techniques have been employed to probe the carrier dynamics (electrons and phonons) in MXenes under optical excitation [35, 36]. These studies focus on the generation and relaxation of hot electrons, and their interactions with phonons on femtoseconds to picoseconds timescales. By investigating electron-phonon coupling and energy transfer pathways through pump-probe data, researchers can achieve a deeper understanding of the fundamental electrons and phonons dynamics of MXenes. Such insights are crucial for optimizing their performance in high-speed optoelectronic devices and photonic systems.

1.1.4 Thermal and thermoelectric properties of MXenes

So far, most research on MXenes has focused on their optical, electrical, electrochemical and mechanical properties. However, experimental research on thermal and thermoelectric transport properties of single- or few-layer MXenes are particularly scarce, with only a few studies focusing on bulk, thin-film MXenes and their composites [37, 38]. On the theoretical side, some studies have investigated the thermal transport and thermoelectric properties of MXenes based on DFT and Boltzmann transport theory. For example, Gholivand et al. calculated the lattice thermal conductivity for monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ MXene and found that O-terminated MXene showed a lower value of $11 \text{ W m}^{-1} \text{ K}^{-1}$ compared to its F-terminated counterpart [39]. Wu et al. used molecular dynamic simulation to investigate the thermal conductivity of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene and the effect of strain on its thermal conductivity [40]. Besides, Kumar et al. theoretically examined key thermoelectric parameters, including the Seebeck coefficient, power factor, and figure of merit (ZT) in monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ MXene [41]. Beyond $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, theoretical simulations of thermal and thermoelectric properties on other types of MXene compounds have been reported, such as oxygen-terminated M_2CO_2 (where $\text{M} = \text{Ti, Zr, Hf, Sc}$) monolayer MXene [27, 42, 43]. Studying MXene single flakes is crucial for understanding the fundamental physics that governs their thermal and thermoelectric behavior at the nanoscale. Unlike bulk materials or thin films, single flakes provide a clear platform to study their inherent transport properties as well as the interplay between two adjacent layers. In addition, these transport properties are critical for applications in thermal management, thermometry, and thermal energy conversion in micro-/nanoscale devices [44, 45]. MXenes exhibit an anisotropic charge transport mechanism that combines a short-range intra-flake band-like conduction with a long-range inter-flake hopping [25]. Key transport parameters, such as electri-

cal conductivity, thermal conductivity, Seebeck coefficient, carrier density and mobility, are often interdependent. These complex transport behaviors underscore the need for more comprehensive experimental studies to better understand their transport properties and the trade-off relationship among these parameters.

However, quantitative measurement of thermal and thermoelectric transport in single MXene flakes are experimentally challenging because of their small flake size ($<10\text{ }\mu\text{m}$ for $\text{Ti}_3\text{C}_2\text{T}_x$, and even $<1\text{ }\mu\text{m}$ for many MXenes compounds) [46, 47]. Controllable stacking or transferring of MXene flakes onto a silicon wafer is the crucial step in studying their transport properties at the monolayer or few-layer scale. In addition, advanced techniques for characterization of their transport properties at the nanoscale are also important. Scanning thermal microscopy (SThM) is a useful tool for local thermometry and heating on 2D flakes [48–50], enabling a fundamental understanding of transport properties of MXenes at the nanoscale. This is of great significance for advancing research and applications of MXenes in thermal management, thermal energy conversion, and temperature sensing.

1.2 Dissertation outline

In this thesis, we aim to experimentally investigate thermal and thermoelectric transport of single MXene flakes. Particularly, we first developed a SThM setup capable of operating in both ambient and vacuum environments. And then we synthesized several kinds of MXene flakes and employed a polymer-assisted dry transfer method to precisely stack flakes to fabricate MXene homostructures. We measure the thickness-/layer-dependent thermal conductance and thermovoltage of MXene by using SThM technique and on-chip thermoelectric devices. Transport parameters of MXene flakes can be further extracted, including electrical conductivity (σ), thermal conductivity (κ) and Seebeck coefficient (S). These results offer

a better understanding of electron phonon interactions, interlayer interactions and the electronic structure of MXenes.

The outline of the dissertation is described in the following. After this introduction chapter, **Chapter 2** will discuss the relevant theory and experiment methods on thermal and thermoelectric transport properties in 2D materials. **Chapter 3** introduces a home-made SThM setup, including its main parts and their working principle. We then describe the synthesis and characterization of several kinds of MXenes, such as $\text{Ti}_3\text{C}_2\text{T}_x$, Mo_2CT_x , and V_2CT_x . In the end, we present the detailed process for fabrication of MXene devices. **Chapter 4** will study the thermal transport of MXenes on SiO_2 substrate via SThM technique. We measure the thickness-dependent thermal conductance between the tip and the flake and then extract the thermal conductivity using a thermal transport model. We further discuss the Wiedemann–Franz Law that related to the electrical and thermal conductivities of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. **Chapter 5** will investigate the thermoelectric transport of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene via both on-chip thermoelectric devices and SThM technique. The interlayer interaction between MXene layers which may affect the Seebeck coefficient are discussed. We also examine the local factors such as defects, strain and surface chemistry that influences the thermoelectric properties. In **Chapter 6**, we summarize the main conclusions and give an outlook for future research.

Chapter 2

Theory and experimental methods

This chapter provides an overview of the theoretical background and experimental methods used to study thermal and thermoelectric transport properties in 2D materials. We discuss the fundamental transport properties and commonly used experimental techniques (especially SThM technique) for investigating thermal and thermoelectric transport in 2D flakes.

2.1 Thermal transport in 2D materials

2.1.1 Fundamentals of thermal transport

A thorough understanding of thermal transport provides the theoretical basis for applications such as thermal management, thermal insulation, and thermoelectrics as well as thermal logic electronics (*e.g.*, thermal rectifiers, thermal transistors, thermal logic gates and thermal memory) [51]. Thermal energy can be transferred through three primary mechanisms: conduction, convection, and radiation. In solids, heat conduction dominates the thermal transport, with

heat carried by lattice vibrations (phonons) and, in metals, also by free electrons. Heat conduction of a solid is typically characterized by thermal conductivity (κ), a fundamental physical parameter that quantifies a material's ability to conduct heat. At the macroscale, heat conduction is governed by Fourier's law, which states that the heat flux (q) is proportional to the temperature gradient (∇T) [52]:

$$q = -\kappa \nabla T \quad (2.1)$$

This law implies that heat flows from regions of higher temperature to lower temperature. For a transient heat conduction, the Fourier–Kirchhoff equation is derived by combining Fourier's law with the energy conservation law:

$$\rho c_p \frac{\partial T}{\partial t} = \nabla(\kappa \nabla T) + \dot{Q} \quad (2.2)$$

where ρ is the density and c_p is the heat capacity of a material, $\dot{Q}$ is the volumetric thermal energy generation rate. In a simple case, when the system has reached thermal equilibrium (steady state), with a temperature-independent κ , and no internal heat generation ($\dot{Q} = 0$), the heat conduction equation reduces to Laplace's equation:

$$\nabla^2 T = 0 \quad (2.3)$$

Once initial and boundary conditions are specified, it can be solved through various analytical and numerical methods depending on geometry and boundary types. These equations correctly describe thermal transport in most practical macroscopic problems.

However, Fourier's law is directly derived from the classical non-equilibrium thermodynamics based on the local equilibrium hypothesis. When heat transport occurs over very short length or time scales, such as in rapid processes or at the micro-/nanoscale, this assumption may no longer be valid. Fourier's law may break down, as non-equilibrium processes are involved. The Boltzmann

transport equation (BTE) offers a useful tool to solve the heat transport problem under these conditions, as described below:

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} f + \mathbf{F} \cdot \nabla_{\mathbf{k}} f = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}} \quad (2.4)$$

where f the phonon distribution function, $\mathbf{v}$ the phonon group velocity, $\mathbf{F}$ the external force and $\left(\frac{\partial f}{\partial t} \right)_{\text{coll}}$ the collision term. Because it accounts for the statistical behavior of phonons and their scattering mechanisms, which provides a more accurate description of thermal transport behaviors, for example size effects, nonlocal and interface thermal transport. Numerical solutions of the BTE have become important in modern semiconductors and thermoelectric devices.

Heat transport is generally via two energy carriers (electrons and phonons) to reach a thermal equilibrium [53]. The total thermal conductivity includes two contributions: the electronic thermal conductivity (κ_e) and the phonon thermal conductivity (κ_{ph}). In metals, the free electrons can be treated as a gas (an electron gas). κ_e is described by the Wiedemann–Franz (WF) law, which relates to its electrical conductivity σ [54]:

$$\kappa_e = \sigma T L_0 \quad (2.5)$$

where T is the absolute temperature, L_0 is the Lorenz number, with a constant value of $2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ in metals. Materials with high electrical conductivity typically also show high thermal conductivity. For example, high electrically conductive silver has a very high thermal conductivity of $429 \text{ W m}^{-1} \text{ K}^{-1}$ [55]. For a given metal material, κ_e can be estimated from the measurement of its σ . However, it is only applicable to classical metals and materials that follow the nearly free electron model. It may be violated at low temperatures or in some strongly correlated systems [56, 57].

Phonons are quantized modes of lattice vibrations. They are the main carriers of heat in non-metallic solids. In a crystalline solid, atoms oscillate around their equilibrium positions, and these

collective oscillations can be described in terms of various normal modes. The normal modes can be described by a dispersion relation $\omega(\mathbf{q}, s)$, where the phonon frequency ω is a function of the wave vector $\mathbf{q}$ and the phonon polarization s . These modes can be classified into low-frequency acoustic modes and high-frequency optical modes. In semiconductors and insulators, phonons contribute to the majority of the heat transport. According to kinetic theory, the thermal conductivity of a real crystal is governed by the frequency dependence of the phonon heat capacity $C(\omega)$, group velocity $\nu(\omega)$, and mean free path (MFP) $\Lambda(\omega)$ [58, 59].

$$\kappa = \frac{1}{3} \int_0^{\omega_m} C(\omega) \nu(\omega) \Lambda(\omega) d\omega \quad (2.6)$$

Phonons can be scattered by defects, boundaries and other phonons (Umklapp scattering) [60]. MFP is an important parameter to characterize the motion of heat carriers. MFP refers to the characteristic distance that heat carriers can transmit thermal energy before undergoing scattering, which can be from several nanometers to several millimeters. The Knudsen number is a crucial parameter defined as the ratio of the phonon MFP and the sample characteristic length L : $K_n = \Lambda/L$. In the diffusive regime, the effective MFP is much shorter than the characteristic length ($K_n < 1$), the Fourier's law is still valid. When the sample length along the transport direction or heat source size becomes comparable to or smaller than the effective MFP ($K_n > 1$), phonon transport becomes ballistic due to the phonon-boundary scattering, leading to strong size effects [61]. This size-dependent ballistic transport sometimes called Casimir effects because it were first considered by Casimir [62]. In nanostructures, thermal conductivity is usually lower than bulk crystals. The high interface and boundary scattering of phonons in low-dimensional materials and thin films can lead to a reduced thermal conductivity. As a result, phonon modes become less effective in carrying heat. For example, the thermal conductivity of silicon decreases with reducing thickness or diameter [63].

In addition, the size effects also happen when the size of the heat source is smaller than the MFP of materials. This situation can occur in a transistor, where most of the heat is generated near the drain due to the self-heating effect, resulting in a nanoscale heat source. Figure 2.1a illustrates the basic physical picture of thermal transport for different heater sizes D . In the diffusive limit ($D \gg \Lambda$), phonons experience enough collisions or scattering to establish a local thermal equilibrium and a continuous temperature gradient during heat dissipation. In this regime, Fourier's law accurately describes the diffusive transport, and the material's thermal conductivity is equal to its bulk value. However, in the ballistic limit ($D \ll \Lambda$), phonons travel ballistically without collisions. In this situation, heat transfer behaves more like thermal radiation, as energy carriers (photons) move directly rather than by successive collisions. Therefore, as the heat source size decreases, the rate of heat dissipation becomes significantly lower than that predicted by Fourier's law, leading to less efficient heat spreading. The contribution of each ballistic phonon mode to the total thermal conductivity is suppressed. As an example, the effective thermal conductivity related with long-MFP ($>1 \mu\text{m}$) phonons of silicon was measured. It shows a heater size dependence normalized effective thermal conductivity (Figure 2.1b). At the heater size $D = 60 \mu\text{m}$, the measured thermal conductivity is close to the bulk value. When D reduces to 30 nm , this measured value becomes only 10% of the bulk silicon.

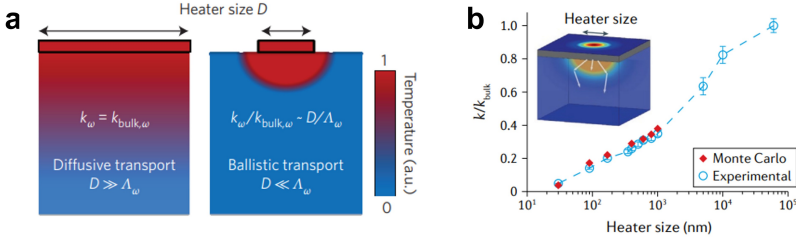


Figure 2.1: (a) Illustration of thermal transport affected by heater size. (b) Dependence of effective thermal conductivity of bulk silicon on the size of the heat source. Figure reproduced from Ref. [64].

Interfaces commonly arise when two different media are joined together, for example, between 2D layered materials and substrates, thin films or at the junctions of semiconductors and metal layers. The interface thermal resistance (also called thermal boundary resistance) R_{int} at the interface between the same or different materials can result in a temperature different at both sides of the interface. The value of R_{int} is given by: $R_{\text{int}} = \frac{\Delta T}{q/A}$, where ΔT is the temperature difference at the interface, q is the heat flux across the interface and A is the cross-sectional area.

Interfaces play an important role in thermal transport, especially at the nanoscale. Kapitza's work in 1941 found a temperature drop at an interface between helium and copper, which creates a thermal resistance [65]. This thermal boundary resistance at interfaces, also known as Kapitza resistance, is basically attributed to a mismatch of the phonon spectrum between two materials in contact. When heat flows across the interface, the incoming phonons will experience reflection and transmission at the interface due to the mismatch in acoustic properties between the two materials. Two classical models that are often used to predict thermal interface conductance: the acoustic-mismatch model (AMM) and the diffuse mismatch model (DMM). The AMM gives the transmission coefficient t_{AB} for phonon energy from material A to material B by assuming that no scattering

happens at solid-solid interfaces [66]:

$$t_{AB} = \frac{4Z_A Z_B}{(Z_A + Z_B)^2} \quad (2.7)$$

where the acoustic impedance is defined as $Z = \rho c$, with c and ρ being the speed of sound and mass density, respectively. This model provides a good approximation for predicting thermal boundary resistance at low temperatures (below 30 K). AMM is applicable to long wavelength phonons, where phonons behave as coherent waves undergoing elastic transport across the interface.

However, due to real interface roughness and disorder, additional phonon scattering occurs. High-frequency phonons exceeding 90 GHz are highly sensitive to interfacial irregularities, leading to diffuse scattering. This behavior is described by the DMM, which assumes that incoming phonons will lose their directional memory upon scattering at the interface. Consequently, the probability of phonon reflection or transmission is determined by the phonon density of states on both sides of the interface. It yields a result that is very close to that of the AMM predictions in some solid-solid interfaces at low temperatures.

2.1.2 Experimental methods in thermal transport measurements

As discussed above, there are many theoretical models that can be used to describe thermal transport and predict thermal conductivity of materials. Unlike the bulk materials, phonons in layered 2D materials are often in a highly non-equilibrium state near interfaces and across thin films, which makes it difficult to define a local temperature [58]. Therefore, Fourier's law may fail to accurately describe their thermal transport behavior. To address this problem, methods such as the BTE [67], molecular dynamics (MD) simulations [68], and the non-equilibrium Green's function (NEGF) approach

[69] have been employed to investigate their thermal transport properties. However, experimentally studying the thermal transport of 2D materials is challenging due to their small size and the difficulty in extracting the heat flux and temperature gradient across the sample. To gain insight into heat transport in 2D materials, there are several electrical and optical techniques available.

Electrical methods: The suspended micro-bridge method [70] was first developed to measure the thermal conductivity of carbon nanotubes and was recently extended to 2D materials, such as graphene [71], BP [72] and MoS₂ [73]. A micro-bridge device is fabricated with two suspended silicon nitride (SiN_x) membranes that are patterned with thin metal heaters and sensors, such as gold lines or platinum (Pt) resistors. It enables precise thermal conductivity measurements at the micro- and nanoscale. Figure 2.2a shows the schematic of the micro-bridge device and its measurement principle. The two suspended membranes are referred to as the heating and sensing membranes. The temperature difference between the two membranes is generated by Joule heating in the Pt resistor, and the resulting heat flux propagates across the sample. By understanding the heat dissipation pathways and analyzing the thermal resistance circuit, one can extract the thermal conductivity of the sample. In addition to thermal measurements, it can also be used to simultaneously measure the Seebeck coefficient and electrical conductivity.

Although micro-bridge method provides a useful platform for measuring the in-plane thermal conductivity of 2D materials, it still faces several limitations. First, the suspended device requires complicated fabrication process and is very fragile. Transferring 2D flakes on device via polymer-assisted methods is likely to damage its delicate architecture or introduce polymer residues, which may affect the measurement accuracy. In addition, the temperature distribution cannot be obtained because the size of Pt heater is much smaller than the sensor membrane. In other words, only the average temperature of the membrane is detectable rather than a spatially

resolved temperature profile over the membranes. Another major challenge is the difficulty in accurately determining the thermal interface conductance between the membrane and the 2D sample, which can introduce additional uncertainty in extracting the intrinsic thermal conductivity.

The 3ω method was developed in the early 1990s by Cahill [74] and is commonly used to measure the thermal properties of materials, particularly thin films. A single metal line is placed on the material and used as both the heater and thermometer for the measurements. An AC current at the frequency of ω is applied to the metal line. The Joule heating of the metal line results in temperature oscillations at the second harmonic 2ω . So the resistance changes of the metal line can be detected at the third harmonic 3ω . Although this method can achieve very accurate thermal property measurement for isotropic thin films, it is less suitable for low-dimensional materials with anisotropic thermal transport. Specifically, the method lacks sufficient sensitivity to distinguish between in-plane and cross-plane thermal conductivity. Moreover, when applied to 2D materials with low heat capacity and thermal conductivity, the signal-to-noise ratio becomes very low due to the weak output signal.

Optical methods (thermoreflectance and Raman): Optical techniques, such as thermoreflectance and Raman spectroscopy, are versatile and powerful tools for measuring the thermal conductivity of 2D materials. The thermoreflectance family consists of time-domain thermoreflectance (TDTR) [75], frequency-domain thermoreflectance (FDTR) [76] and thermoreflectance thermal imaging (TRI) [77]. TDTR is widely used to measure the thermal conductivity of thin films and the thermal interface conductance between dissimilar material layers. It employs a laser pump-probe technique that a pump pulse heats the sample, while the delayed probe pulse measures the change in thermoreflectance as a function of time delay between the pump and probe pulse arrivals. It shows high temporal resolution of nanoseconds due to its femtosecond laser pulses. TDTR

can be used to not only measure heat transport in 2D materials, but also the thermal interface resistance between the 2D materials and substrate [78]. In contrast, FDTR operates by modulating the pump laser at different frequencies and analyzes the phase response of the signal. Its systems are typically easier to set up and maintain than TDTR. A charge-coupled device (CCD) camera was used for TRI, which enables the rapid visualization of plasmonic heating with sub-micron spatial resolution. TRI provides 2D thermal maps of the absolute temperature rise. The temperature rise at each pixel was calculated by correlating the measured reflectivity change by CCD with the calibrated thermorefectance coefficient. Figure 2.2b shows an example of imaging quasi-ballistic thermal transport of InGaAs devices by using TRI [77]. However, thermorefectance methods have drawbacks for single MXene flakes. MXenes are generally produced as small flakes with limited lateral size, typically on the order of a few micrometers or less. The relatively large laser spot size used in thermorefectance techniques can cause significant heat spreading into the substrate and surrounding areas and make it difficult to accurately extract the intrinsic thermal properties of the MXene flake.

Another optical technique, Raman thermometry, has become an important experimental method for characterizing the thermal energy transport of 2D materials. It detects the shift in Raman peaks as a function of temperature or thickness of layered 2D materials [79]. Figure 2.2c shows the schematic of the experiment on a suspended single-layer graphene, which is performed using the confocal micro-Raman spectroscopy. A small laser spot ($0.5\text{ }\mu\text{m}$ to $1.0\text{ }\mu\text{m}$) was used to heat the sample, then the heat is propagating radially to the edges. By measuring excitation power dependence of the Raman shift of G peak, the thermal conductivity of graphene can be extracted. This Raman technique is also used to measure the thermal conductivity of other 2D materials such as hBN [80], MoS₂ [81] and BP [82]. However, using Raman spectroscopy for thermal measurements requires that 2D materials absorb the excitation

laser. Some 2D materials do not exhibit strong or clear Raman peaks, which limits the applicability of this method. For example, MXenes typically exhibit weak Raman signals and show negligible Raman peak shifts with changes in temperature or thickness [83]. In addition, all optical techniques face a significant challenge in spatial resolution due to the fundamental diffraction limit. According to the Rayleigh criterion ($\theta = 1.22\lambda/D$, where θ is the minimum resolvable angle, λ is the wavelength and D is the characteristic size of the optical system), it is difficult to achieve the resolution smaller than 100 nm.

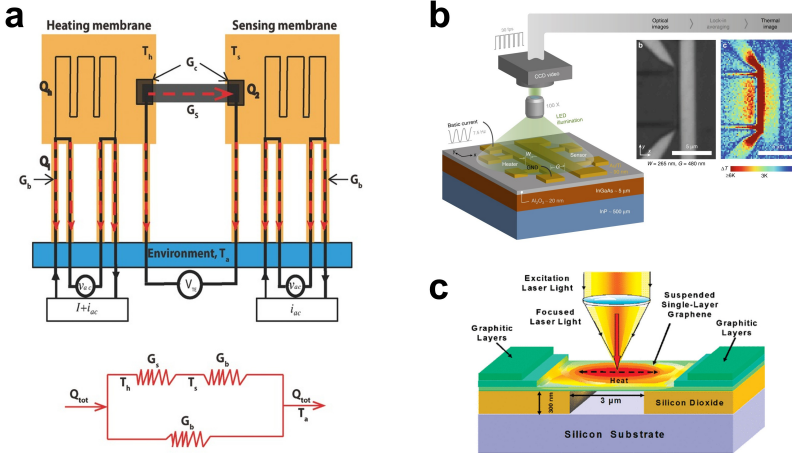


Figure 2.2: Schematics of thermal conductivity measurement techniques for 2D materials. (a) Suspended micro-bridge method. (b) Thermoreflectance methods. (c) Photothermal Raman technique with laser focused on the suspended sample. Figure reproduced from Refs. [77, 79, 84].

SThM technique: We reviewed the current theory and experiments methods on thermal transport, and there are many challenges for nanoscale thermal transport measurements nowadays. Considering the anisotropic nature of 2D materials and local factors, such

as defects (wrinkles, bubbles), strain, substrates can influence the thermal transport in 2D flakes. SThM, with its high spatial resolution on the order of tens of nanometers, offers a powerful technique for local thermal measurements. It has the capability to map the thermal conductance of the sample and detect local variations in heat transport across it. This can offer deeper insight into the underlying factors contributing to heat transfer. To date, SThM has become a fundamental and essential technique to characterize thermal transport at the micro-/nanoscale [85–88]. In this section, we will review the development and working principles of SThM, as well as the analytical methods for quantitative nanoscale thermal measurements.

The atomic force microscope (AFM) was developed by Binnig et al. [89] in 1986 based on the principles of scanning tunnelling microscope (STM) developed in 1981 [90] and the stylus profilometer developed in the 1940s [91]. Since the STM relies on electron tunneling between the tip and the sample surface, the sample must be conductive. This limitation is overcome by AFM, which can be used for many surfaces such as conductors and insulators by measuring the interatomic forces. The AFM keeps a constant interatomic force by varying the tip-sample distance through its feedback system, enabling it to accurately map the topography of a sample surface. Since then, many scanning probe microscopy (SPM) techniques based on AFM or STM have been developed and applied not only for imaging surface topography, but also for mapping various physical properties of materials, including their electrical, mechanical, and thermal characteristics [92, 93].

The first SPM setup using thermal phenomena was invented by Williams and Wickramasinghe in 1986 and was called the scanning thermal profiler (STP) [94]. The probe has a heated thermocouple sensor at the tip apex, the heat flux between the probe and the sample was used as the feedback mechanism for controlling the tip-sample distance. Although STP was an extension method for imaging topography to insulators, it did not design for thermal

imaging. In the following years, SThM systems were further developed to enable the simultaneous collection of thermal images and topography. Subsequent research focused on the development of advanced SThM probes to achieve more accurate, faster and higher-resolution nanoscale thermal measurements. These probes evolved from simple thermocouple junctions to metal resistive thermal probes, such as Wollaston wire probes, and later to smaller, more sensitive AFM-based designs like Palladium (Pd)/SiN_x probes and doped silicon probes [87, 88]. Today, the latest SThM technique can be employed to study local temperature rises and to characterize the thermal conductivity and the Seebeck coefficient of a material. Figure 2.3 describes the setup of a typical SThM system. It consists of the following main parts: i) A SThM probe that can be worked both as a temperature sensor and a heat source; ii) feedback loop systems, including cantilever deflection detection and piezoelectric scanners; iii) data acquisition and signal processing for control units and collection of experimental data. Since the output signal of the SThM is usually very small, a Wheatstone bridge circuit is employed to amplify the signal and improve the signal-to-noise ratio.

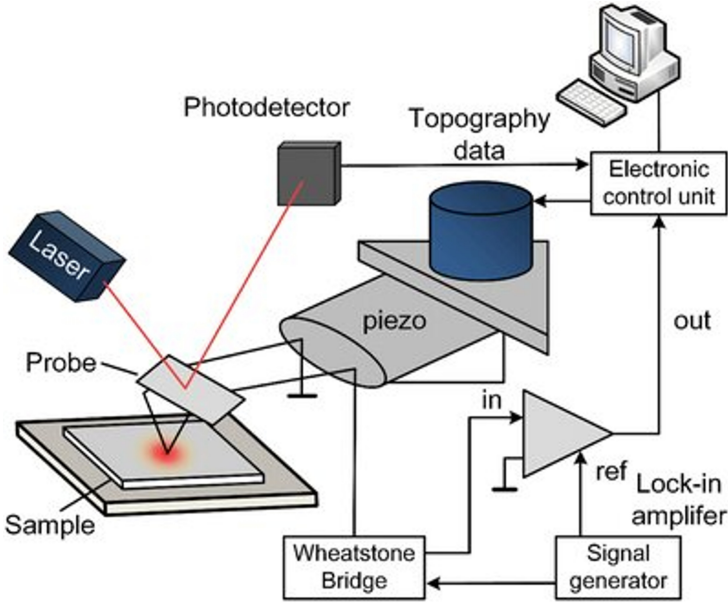


Figure 2.3: Schematic diagram of standard SThM setup which includes a thermoresistive probe and a Wheatstone bridge circuit in an AFM platform. Laser feedback is used to detect the deflection of the cantilever. Figure reproduced from Ref. [87].

Thermal probes are the key components of SThM systems that determine the thermal measurement performance. The crucial parameters of an SThM probe include the probe type (thermoelectric or resistive), tip radius, and probe material. Thermal probes are commonly categorized based on their sensing mechanisms, including thermocouple, resistive, thermal expansion, fluorescence-based types and so on. In this section, a short introduction to the first two categories will be presented, while the others will not be explored in detail.

Thermocouple probes: Thermocouple probes are based on the thermovoltage generated at the junction between two different electrodes due to the thermoelectric effect. This thermocouple junction

can be established between the tip and sample surface through the non-contact and point contact modes. For example, Sadat et al. [95] reported a thermojunction formed between a Pt tip and a metallic surface, which they used to record the temperature field of the surface. However, this method requires an electrically conducting surface, which limits its application. With the rapid development of micro- and nanofabrication technologies, later methods focus on fabricating the probe with a built-in thermocouple sensor (*e.g.*, Au-Pd, Au-Chromium (Cr) junction, Figure 2.4a). As shown in Figure 2.4b, Kim et al. [96] designed a thermocouple probe with a small Au-Cr junction at the tip apex. This probe can be used for quantitative temperature measurements, as the thermovoltage generated at the Au-Cr junction is directly correlated with the local temperature of the sample. The probe was fabricated with a small tip radius (around 10 nm) to enhance both spatial resolution and response time, achieving a temperature resolution of approximately 15 mK.

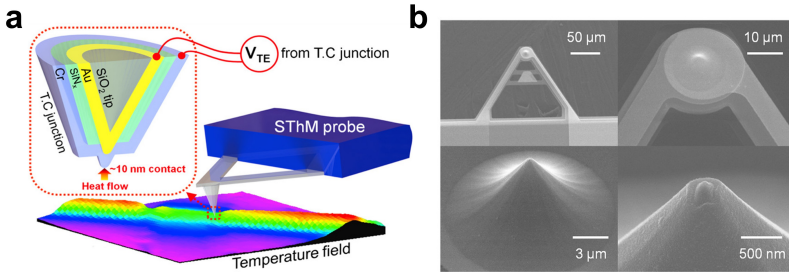


Figure 2.4: (a) Schematic illustrating the SThM technique with an Au-Cr thermocouple junction at the end of the tip. The thermovoltage generated from thermocouple is directly proportional to the local temperature of the sample. (b) SEM images of the SThM probe with an Au-Cr thermocouple at the apex. Figure reproduced from Ref. [96].

Thermoresistive probes: Thermoresistive probes are, based on

resistance thermometry, use a resistor as a thermal sensor (*e.g.*, metal thin films, wires and highly doped silicon). Pt and Pd are commonly used thermal sensors due to their high temperature coefficient of resistance (α) and high sensitivity. This type of probe can be served as both thermometry and a local heater for thermal-related properties measurements. In thermometry mode, a small current is applied to the probe which can be simultaneously used to heat up the tip and measure a change in its electrical resistance. The working principle is described as the following equation:

$$R_p(T) = R_{p0} (1 + \alpha(T - T_0)) \quad (2.8)$$

where R_{p0} is the probe resistance at a reference temperature T_0 . For the thermoresistive probe, a constant applied power can be used to the probe with a combination of AC+DC bias.

Wollaston wire probes: R. Pylkki et al. [97] proposed the first SThM resistive probe in 1994. As shown in Figure 2.5a, the cantilever of the probe is made of platinum and rhodium (Pt-Rd) alloy coated with a silver (Ag). The Pt-Pd wire was bent into a V-shape and exposed by electrochemical etching to create a sharp resistive tip. This probe has high electrical and mechanical robustness with a spatial resolution of a few microns. However, the relatively large active area limits its effectiveness for thermal measurements at the nanoscale.

Pd probes: To improve the thermometric performance, the size of the Pd sensor is reduced through micro-/nanofabrication. These probes are designed by depositing a Pd sensor on an AFM cantilever. As shown in Figure 2.5b, the probe consists of two gold pads and a V-shaped Pd thin film deposited at the end of the probe. The cantilever is made of Si_3N_4 and has a low spring constant. This tip has a small radius of around 50 nm, a time response of a few tens of microseconds, and a temperature resolution of 0.1 K.

Doped silicon probe: Another special thermoresistive probe is the doped silicon probe, which was first developed by IBM for data-

storage devices and high-speed nanolithography. The probe contains a high-doped U-shaped silicon cantilever and a low-doped resistive region at the tip apex (Figure 2.5c). The tip is made by a regular AFM probe fabrication and has a conical shape with a small apex radius of 10 nm. Unlike the Pd probe, a high current can be applied to the doped silicon probe and lead to a high temperature rise of over 150 K. But high current will cause the non-linear changes in resistance, and we need to consider the high-order corrections. Furthermore, a high vacuum environment is essential for this probe to achieve high resolution, as the sample and sensor/heat source region are separated by the tip.

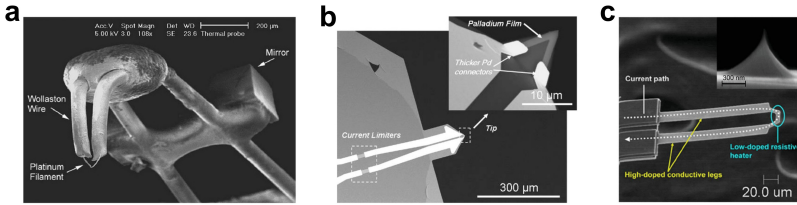


Figure 2.5: SEM images of different types of the SThM probes: (a) A Wollaston probe. (b) Thermoresistive probe with a Pd heater at the end of the tip. (c) Doped silicon probe with two-legs high-doped cantilever and low-doped sharp tip. Figure reproduced from Refs. [48, 98, 99].

In this thesis, resistive probes were used for all experiments due to their dual functionality as both the accurate thermal sensor and local heat source for thermoelectric measurements. Three main applications of the probe are highlighted: thermometry, characterization of thermal conductivity and thermal interface resistance, and for local heating element. To quantitatively investigate the thermal transport properties in a layered 2D material, it is essential to understand the heat-transfer mechanisms at the tip-sample interface and to apply an appropriate analytical thermal model and simulation.

There are various mechanisms of heat transfer between the SThM tip and the sample. Figure 2.6 presents the heat transfer channels from a hot tip to the sample under an ambient environment. In contact mode, these channels include direct heat conduction at the solid-solid contact and through the water meniscus, the heat transfer through the surrounding air and thermal radiation. All these factors will cause an increase in thermal resistance and therefore the total thermal conductance is the sum of these contributions. The effective thermal resistance R_{th} (or thermal conductance G_{th}) describing the tip-sample thermal interaction was defined by Majumdar [100]:

$$R_{\text{th}} = \frac{1}{G_{\text{th}}} = \frac{1}{G_{\text{ss}} + G_{\text{w}} + G_{\text{air}} + G_{\text{rad}}} \quad (2.9)$$

where G_{ss} , G_{w} , G_{air} and G_{rad} are the thermal conductances describing the probe-sample thermal transfer through the solid-solid contact, water meniscus conduction, gas conduction and radiation, respectively. The SThM output signal primarily depends on these factors. This is a complex system between the probe and the sample. In real experiments, it is important to account for them and apply appropriate data corrections to obtain accurate results.

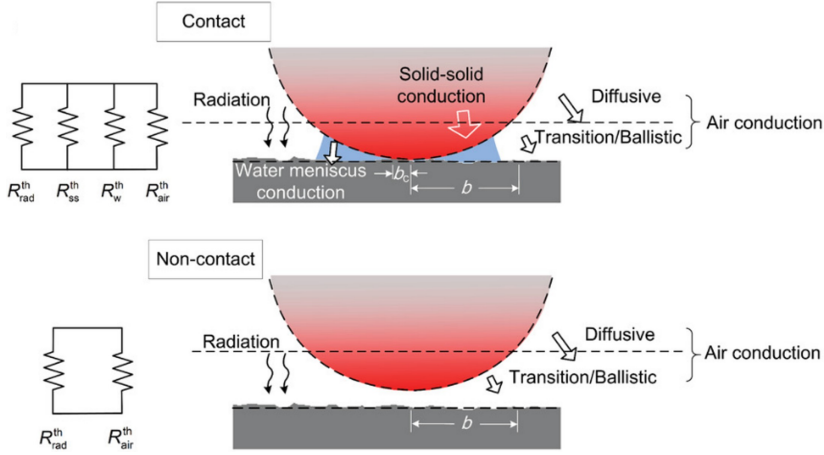


Figure 2.6: The probe-sample interface showing the different heat transfer mechanisms and the total thermal conductance involved in the contact and non-contact modes. Figure reproduced from Ref. [87].

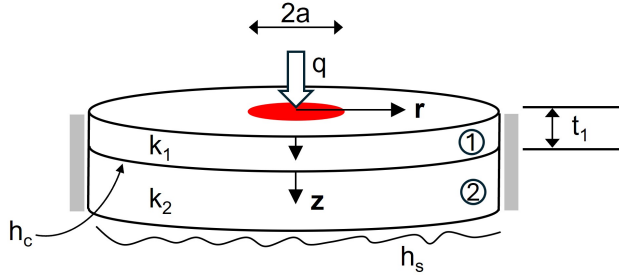


Figure 2.7: Model of a heating spot with a radius of a on a film of thickness of t_1 on a substrate. Figure reproduced from Ref. [101].

SThM measures the total thermal resistances, while other thermal parameters such as thermal conductivity and thermal interface conductance can be extracted through modeling methods, including finite element analysis and analytical formulations. However, the

resulting values are considered effective quantities, as the models may not fully capture the actual physics of the system. An effective analytical thermal model for quantitatively investigating thermal spreading in layered 2D materials was developed by Muzychka and Spiece [49, 101]. This model uses cylindrical symmetry and a point heat source with a radius of a . The top layer material 1 has a thickness t and thermal conductivity k_1 , which is placed on the substrate of material 2 with a thermal conductivity k_2 (Figure 2.7).

The detailed solution process is not described here. The solution for the thermal spreading resistance of a layer on substrate for an isotropic heat transport is expressed as:

$$R_{\text{spr}} = \frac{1}{\pi k_1 a} \int_0^\infty \left[\frac{1 + K \exp\left(-\frac{2\xi t_{\text{eff}}}{a}\right)}{1 - K \exp\left(-\frac{2\xi t_{\text{eff}}}{a}\right)} \right] J_1(\xi) \sin(\xi) \frac{d\xi}{\xi^2} \quad (2.10)$$

where J_1 is the 1st order Bessel function of the first kind and ξ is the integration variable. Considering the interfacial thermal resistivity between the top layer and the substrate, denoted as r_{int} , the effective thickness t_{eff} rather than the actual physical thickness of the top layer is used. K and t_{eff} are defined as:

$$K = \frac{1 - k_2/k_1}{1 + k_2/k_1} \quad (2.11)$$

$$t_{\text{eff}} = t + r_{\text{int}} k_1 \quad (2.12)$$

However, in layered 2D materials, thermal transport is typically anisotropic with different in-plane (k_{xy}) and cross-plane (k_z) thermal conductivities. Equation 1.10 is modified to account for the anisotropic heat transport by Muzychka. The thickness t of the top layer is replaced by an average thickness t_a and the thermal conductivity k_1 is replaced by an average value k_a :

$$t_a = \frac{t}{\sqrt{k_z/k_{xy}}} \quad (2.13)$$

$$k_a = \sqrt{k_{xy} k_z} \quad (2.14)$$

This analytical model allows us to understand how the sample and probe parameters affect the measured thermal resistance. It also can be directly applied to SThM experimental results to extract the thermal conductivities and thermal interface conductance of 2D layers on substrate. For example, Gonzalez-Munoz et al. measured the anisotropic thermal transport in γ -InSe on Si substrate using SThM, low anisotropic thermal conductivities of $k_{xy} = 2.16 \text{ W m}^{-1} \text{ K}^{-1}$ in-plane and $k_z = 0.89 \text{ W m}^{-1} \text{ K}^{-1}$ cross-plane were extracted via the above thermal transport model [49]. Besides, Spiece et al. studied the thermal transport in franckeite with different number of layers using SThM. The thermal conductivity was extracted using this analytical model [102]. Similar quantitative thermal measurements also have been conducted on other 2D materials, such as graphene [103] and MoS₂ [104].

2.2 Thermoelectric transport properties in 2D materials

2.2.1 Fundamentals of thermoelectric transport

The Seebeck effect is a phenomenon that the conversion of a temperature gradient into an electrical current inside one material or at a junction between two different materials. The first thermoelectric phenomenon was discovered by Thomas Johann Seebeck in 1821. He observed the deflection of a compass magnet when heating the junction formed by two dissimilar materials [105]. In the case of an open circuit, Seebeck coefficient is defined as the ratio of the generated voltage and the applied temperature difference, and is measured in V/K.

$$S = -\frac{\Delta V}{\Delta T} \quad (2.15)$$

Similarly, the reverse of the Seebeck effect is discovered by Jean-Charles Peltier in 1834, called the Peltier effect. He observed a heating or cooling when an electrical current is passed through a thermocouple [106]. The Peltier effect and Seebeck effect are related by the Onsager reciprocity relation, so the Peltier coefficient Π at temperature T is given by:

$$\Pi = ST \quad (2.16)$$

One can simply evaluate the Peltier coefficient of a material from its Seebeck coefficient.

Figure 2.8 shows the Seebeck effect and it's a simple setup we can use to measure the Seebeck coefficient of a material. When a material is placed in a thermal gradient (one side is heated up to temperature T_h and the other side is at Temperature T_c , which generated a temperature different $\Delta T = T_h - T_c$ across the material), the charge carriers (electrons and holes) gain more energy on the hot side and tend to diffuse toward the cold side. There is a net flow of charge carriers from the hot side to the cold side inside the material. This movement of charge carriers generates a voltage difference $\Delta V = V_a - V_b$ across the sample. Electrical and thermal conductivity are always positive and cannot change sign, but Seebeck coefficient can be either positive or negative which depends on the nature of charge carriers. The Seebeck coefficient is negative when charge transport is electron-like ($S < 0$), or positive when charge transport is hole-like ($S > 0$). However, electrons in noble or most alkali metals, such as copper, silver, gold and lithium, behave like a nearly free electron gas, but they have the “wrong” sign of the Seebeck coefficient: it is positive like a gas of hole-like particles [107, 108].

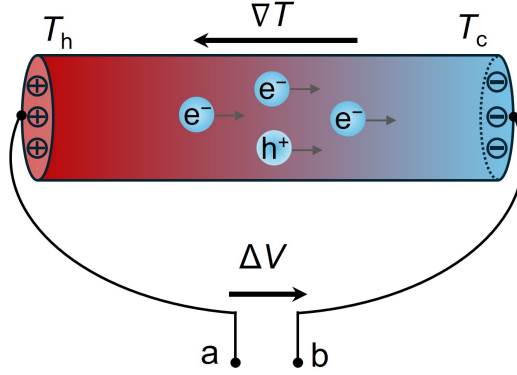


Figure 2.8: Schematic of the Seebeck effect and Seebeck coefficient measurements. Under a temperature gradient, the carriers move from the hot side to cold side, a voltage drop (thermovoltage) can be measured between these two sides.

To further understand the behavior of the Seebeck effect, we need to consider the Fermi-Dirac (F-D) distribution $f(\varepsilon)$ of electrons.

$$f(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{k_B T}\right) + 1} \quad (2.17)$$

where μ is the chemical potential, k_B the Boltzmann constant, T the temperature and ε the energy. The thermoelectric diffusion originates from the difference in the F-D distribution between the hot and cold sides. As shown in Figure 2.9, the F-D distribution becomes broadened on the hot side and narrower on the cold side when applying a temperature gradient along a material. On the hot side, the occupation probability increases for high-energy states and decreases for low-energy states, and it is reverse for the cold side.

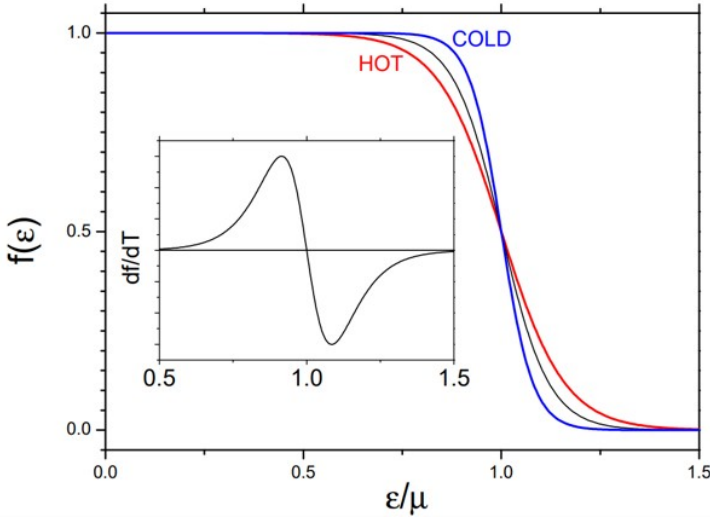


Figure 2.9: The F-D distribution broadens at the hot side. This asymmetric F-D distribution induces the carrier's diffusion between the hot side and the cold side. The inset shows its temperature derivative. Figure reproduced from Ref. [109].

Boltzmann transport theory provides a general framework for understanding of the Seebeck coefficient of the diffusion thermoelectrics, which is expressed by Mott's equation [110]:

$$S = \frac{\pi^2}{3} \frac{k_B^2 T}{e} \left. \frac{d \ln \sigma(E)}{dE} \right|_{E=E_F} \quad (2.18)$$

where e the elementary electronic charge, $\sigma(E)$ the energy dependent conductivity and E_F the Fermi energy. This equation shows a relation between the Seebeck coefficient and the electrical conductivity and is the most used equation in thermoelectrics. The Seebeck coefficient varies depending on the energy dependence of carrier transmission above and below the Fermi level. Considering the Drude model, the energy-dependent electrical conductivity at Fermi energy can be expressed as: $\sigma(E) = n(E) e \mu(E)$ [111], which

is related to the carrier density $n(E)$ and charge mobility $\mu(E)$ at the energy level E . Substituting it into Mott's formula gives the following equation:

$$S = \frac{\pi^2 k_B^2 T}{3 e} \left[\frac{1}{n(E)} \frac{dn(E)}{dE} + \frac{1}{\mu(E)} \frac{d\mu(E)}{dE} \right] \Big|_{E=E_F} \quad (2.19)$$

The Seebeck coefficient of a material reflects the asymmetry in the electronic structure and scattering rates near the Fermi level. Equation 2.18 clearly shows that the Seebeck coefficient can be increased through two mechanisms: (i) based on $n(E) = g(E) f(E)$, where $g(E)$ is density of states (DOS) and $f(E)$ the Fermi function, an increased in energy-dependent $n(E)$, particularly by a local increase in $g(E)$ can lead to a larger Seebeck coefficient. (ii) according to $\mu(E) = \frac{e\tau(E)}{m^*}$, where $\tau(E)$ is the relaxation time and m^* the effective mass, the stronger energy-dependent $\mu(E)$ or $\tau(E)$, such as that introduced by an enhanced scattering mechanism, also contributes to an increased Seebeck coefficient. As a fundamental physical parameter, Seebeck coefficient links the electronic structure and transport parameters. Thermoelectric transport studies provide deeper insight into this relationship and help optimize the performance of thermoelectric devices by band structure and transport engineering.

The efficiency of a thermoelectric device is measured by three combinatorial material parameters. This dimensionless figure of merit (ZT) is defined as:

$$ZT = \frac{S^2 \sigma T}{\kappa} = \frac{S^2 \sigma T}{\kappa_e + \kappa_{ph}} \quad (2.20)$$

To achieve a high ZT value, one can maximize both the Seebeck coefficient and electrical conductivity while minimizing the thermal conductivity. However, the optimization of these three parameters to realize a high ZT has become challenging due to their trade-off relation. As shown in Figure 2.10, these three parameters are

dependent on the band structure and carrier concentration of a material. The transport coefficients, particularly S and σ exhibit an inverse relationship, making it difficult to increase one without decreasing the other. Meanwhile, the electronic thermal conductivity κ_e will also increase with increasing the σ according to the WF law. As a result, conventional bulk thermoelectric materials face intrinsic limitations to achieve a very high ZT ($ZT > 2$). To date, a record $ZT = 2.6 \pm 0.26$ has been reported in a single-crystalline $\text{Bi}_{88}\text{Sb}_{12}$ topological insulator [112], which is primarily attributed to the one-dimensional Landau level quantization enhancement.

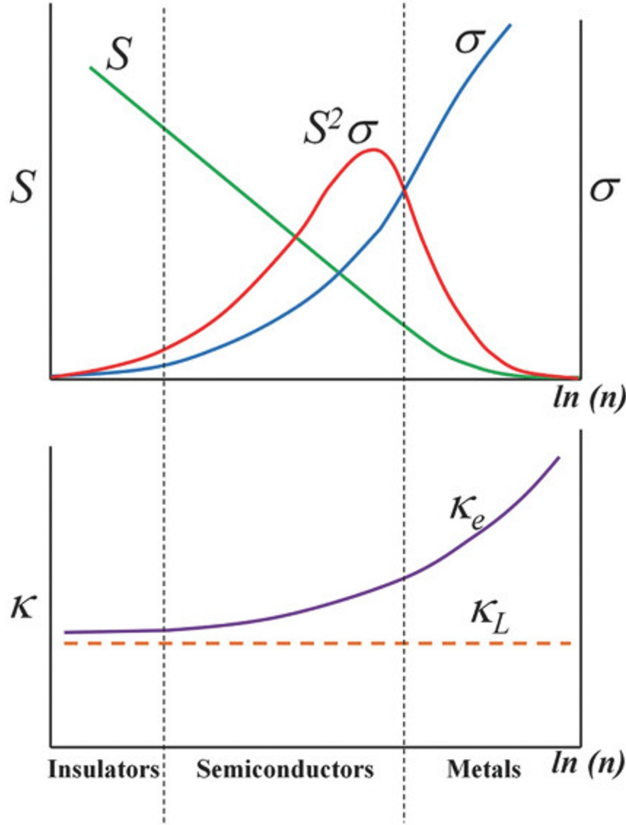


Figure 2.10: Illustration of the variation of S , σ , power factor $S^2\sigma$, κ_e and κ_l as a function of the concentration of charge carriers n . Figure reproduced from Ref. [113].

In 1993, Hicks and Dresselhaus [114, 115] predicted that nanostructures could alter the band structure and improve ZT on the modeling of thin films and nanowires. Electrons are confined to a small physical space in low dimension, leading to a sharp DOS transition at the band edges with respect to energy. Later studies [116] show that nanostructures also introduce strong boundaries and interface scattering. For 2D case, Seebeck coefficient and ZT

may be varied both by doping and by changing the layer thickness [117]. In general, it is possible to decouple these parameters S , σ , and κ by careful structure manipulation [118]. A sharp DOS profile is expected in layered 2D materials, and their transport properties can be tuned by the van der Waals interfaces, such as interlayer interactions [119, 120]. Nanostructuring and stacking 2D flakes can yield numerous possibilities for tuning thermoelectric properties [121].

2.2.2 Experimental methods of thermoelectric transport measurements

Layered 2D materials often show unique electronic structures that differ significantly from their bulk counterparts due to the quantum confinement effects [122]. Studying thermoelectric transport properties in monolayer or few-layer materials is crucial for understanding the underlying physical mechanism behind their thermoelectric effect. When the flakes size is down to the micro/nanoscale, conventional thermoelectric measurement techniques are no longer applicable. Instead, specialized methods that generate micro/nanoscale heat sources are required. To measure the Seebeck coefficient of a material, we basically need to create a temperature gradient along the sample and then a thermoelectric voltage V_{th} will be generated along this temperature gradient. Therefore, accurate measurements of the Seebeck coefficient require the knowledge of the temperature distribution (or temperature different ΔT) between two electrodes and the resulting V_{th} . We will review the state-of-the-art techniques commonly used to measure the thermoelectric transport properties of layered 2D materials.

One technique is the thermoelectric micro-device platform. Figure 2.11 shows the typical structure of thermoelectric micro-bridge devices for Seebeck coefficient and ZT measurements. For the supported one (Figure 2.11a), this micro-device is typically patterned

onto a silicon substrate coated with a thin silicon oxide (SiO_2) layer via electron beam lithography and metal deposition processes. The metal electrodes (usually Au/Cr or Au/Ti) are deposited as both thermometers and source and drain contacts for thermovoltage measurement. One or two micro-heaters are fabricated nearby to create a temperature difference between the source and drain contacts. The geometry of the device can be designed based on the size of the flakes. The thin flakes can be precisely transferred on this micro-device through the commonly used dry-transfer methods [123]. The supported thermoelectric micro-device can only simultaneously measure the Seebeck coefficient and the electrical conductivity of a flake. However, if we want to evaluate the ZT of 2D materials, the suspended micro-bridge (Figure 2.11b) can be used to accurately measure the thermal conductivity and therefore calculate their ZT value. By using these thermoelectric micro-devices, the thermoelectric transport properties of single-layer or few-layer 2D materials (especially graphene, BP and TMDs) have been widely investigated recently [124]. For example, several measurements of graphene showed that the Seebeck coefficient changes at various temperatures and gate voltages [125]. Because graphene is an intrinsic semimetal with a Dirac cone-like band structure, the sign of the Seebeck coefficient changes at the charge neutrality point (CNP) as the majority carrier density switches from electron to hole. As a result, the Seebeck coefficient showed an antisymmetric dependence on carrier density. Furthermore, the vdW interactions between two graphene flakes in a moiré superlattice have attracted increasing attention in recent years, as they significantly influence thermoelectric transport behavior. Several studies have investigated the thermoelectricity of twisted bilayer graphene (tBLG) using thermoelectric micro-devices [126–128]. At small twist angles ($<1.6^\circ$), tBLG showed abnormal thermoelectric transport behavior, including a violation of the semiclassical Mott relation [126]. Thermoelectric micro-device is an accurate and stable method that provides a qualitative understanding of the overall thermoelectric transport behavior

in 2D materials, which helps to understand the impact of interlayer and electron–phonon interaction on thermoelectric transport of 2D materials. The tunability of the Seebeck coefficient at vdW interfaces offers a novel approach to optimizing the thermoelectric properties of layered 2D materials.

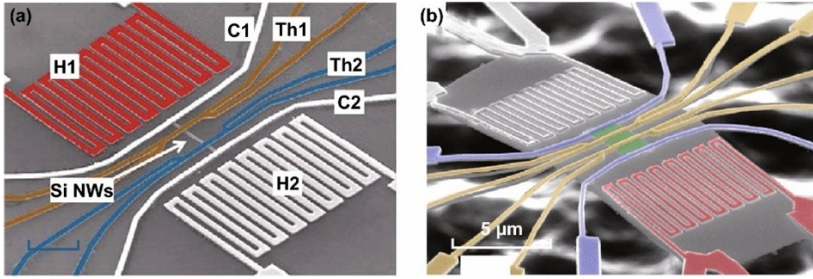


Figure 2.11: (a) supported (b) suspended thermoelectric micro-bridge device. Figure reproduced from Ref. [129].

When a material absorbs photons, particularly infrared or laser radiation, the energy is converted into heat and causes a local temperature rise. Therefore, laser heating is also a powerful approach as a heat source to induce a localized temperature gradient within a 2D flake, leading to a generated thermoelectric voltage or current via the Seebeck effect. This photothermoelectric effect has been studied in several semiconducting 2D materials, such as graphene [130] and TMDs [131, 132]. Combined with scanning photocurrent microscopy or scanning near-field optical microscopy (SNOM) enables high-resolution mapping of thermoelectric properties at the nanoscale. For example, graphene, BP and MoS₂ have demonstrated strong photothermoelectric responses under the focused laser spot. The photothermoelectric properties of MoS₂ flakes were studied via scanning photocurrent microscopy. Local heating at contact junctions or edges induced a measurable photocurrent signal, resulting in a large and gate-tunable Seebeck coefficient was observed [131]. Due to the diffraction limit, scanning photocurrent microscopy can-

not achieve sub-nanometer spatial resolution. As a scanning probe microscopy technique, SNOM surpasses the diffraction limit and enables high-resolution imaging down to the atomic scale, which allows locally measure the thermoelectric transport at the nanoscale. For example, SNOM can be used to map the photothermoelectric response in tBLG device within the moiré domains [133]. A triangular pattern of photocurrent, consistent with the moiré periodicity, was observed, highlighting the spatial modulation of thermoelectric properties induced by the moiré superlattice.

Another scanning probe microscopy technique, SThM has also been employed to study local thermoelectric transport. Because the Seebeck effect is driven by heat-induced electron diffusion, local thermoelectric imaging provides insight into the coherent electron and heat transport at the nanoscale. While the global thermoelectric transport properties of 2D materials have been widely reported, their local thermoelectric effects remain relatively unexplored. Similar to thermal transport, thermoelectric transport in 2D materials is sensitive to various factors including defects, strain, geometry and substrate effect, especially when their thickness is reduced to monolayer or just a few layers due to their large surface-to-volume ratio. For MXenes, surface chemistry is also an important factor. These factors can locally alter their electronic band structure or scattering mechanisms and therefore influence their transport properties. For example, substrate effects are important to consider since most 2D materials are commonly supported on SiO_2 substrate during device fabrication and measurements. Previous studies [134, 135] showed that graphene flakes placed on a SiO_2 substrate can cause inhomogeneous charge carrier density, the so-called charge puddles. This effect also will cause the spatial Seebeck variation at the nanoscale. Thermoelectric puddles of graphene have been investigated using SPM techniques (*e.g.*, SThM [50], scanning thermoelectric microscopy (SThEM) [136, 137]). For example, Figure 2.12a shows the local thermovoltage mapping on graphene channel under the different gate voltages. In p-doped graphene, the

majority carriers are holes, while in n-doped graphene, the majority carriers are electrons. Therefore, the polarity of the thermovoltage is opposite for p-type and n-type doping at the contacts. A strong chaotic signal around the CNP is attributed to the charge puddles which locally changes the carrier concentration of graphene. The Seebeck coefficient map is also reconstructed via a deconvolution method. In addition, local measurements on twisted graphene at small twist angles enable observation of the thermoelectric response across different stacking orders. The twisted graphene consists of three lattice configurations: AA, AB/BA, and saddle point (SP). As shown in Figure 2.12b, the Seebeck difference among AA, AB/BA and SP stacking orders varies with the gate bias, leading to different thermovoltage contrasts across the junctions. By studying the inhomogeneous thermovoltage response at the nanoscale, we can gain a further understanding of how local factors influence thermoelectric transport behavior, thereby improving our insight into the electronic structure and scattering mechanisms of 2D layered materials.

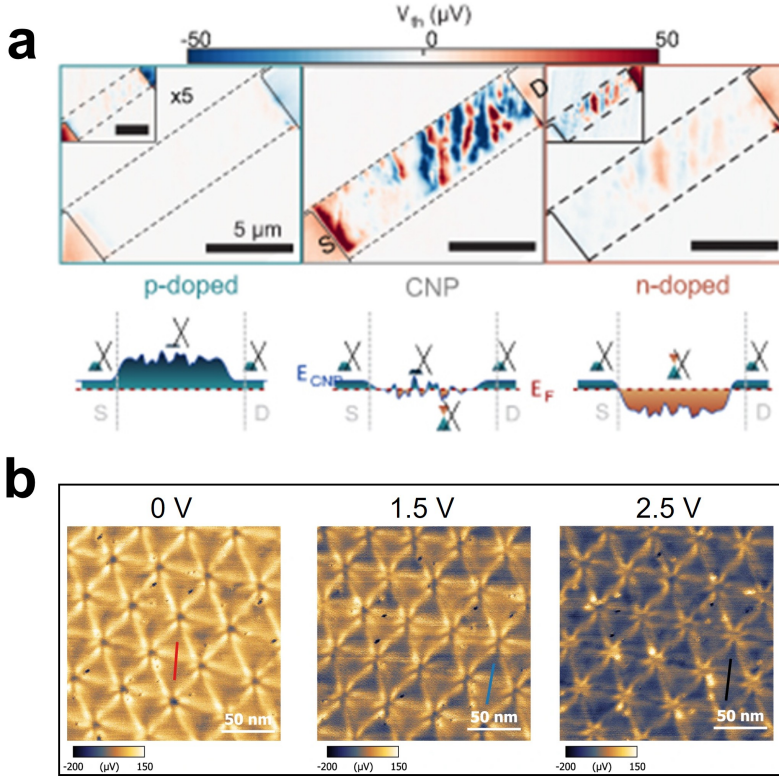


Figure 2.12: (a) Thermovoltage maps in single layer graphene channel at three different gate voltages. (b) Thermovoltage maps in twisted graphene with a twist angle of 0.28° at gate voltages of 0, 1.5, and 2.5 V, respectively. Figure reproduced from Refs. [50, 137].

2.3 Summary

In this chapter, we review the fundamental theory and experimental methods for thermal and thermoelectric transport in 2D materials. Various techniques have been developed to measure the transport properties in nanoscale systems. SThM technique shows its advantages to address the commonly faced challenges of standard methods.

We demonstrate the versatility of SThM as a tool for local thermal and thermoelectric analysis, including the quantitative characterization of local thermal resistance, interfacial thermal resistance and anisotropic thermal conductivity and Seebeck coefficient in 2D materials. SThM requires theoretical understanding and appropriate modeling methods to achieve quantitative measurements. In the following chapter, we will describe the SThM experimental setup and the methodology adopted in this thesis.

Chapter 3

Building a SThM setup and MXene device fabrication

In this chapter, we will focus on our customized SThM system and its measurement principles, as well as the MXene device fabrication process. We will quantitatively measure thermal and thermoelectric transport properties of single- and few-layer MXene flakes using SThM technique and on-chip thermoelectric micro-devices. The thermal conductivity is extracted from thermal resistance maps via a thermal transport model and Seebeck variation profiles are obtained from thermovoltage maps via the deconvolution method. These methods for thermal and thermoelectric transport measurements in single MXene flakes are presented.

3.1 Building a SThM setup

Figure 3.1 provides a global overview of the SThM setup that we have built. Our SThM is based on a Thorlabs' AFM platform with a thermal probe and other electronic parts (Wheatstone bridge, breakout box, wave generator, pre-amplifier and lock-in amplifier). This SThM enables us to simultaneously measure the topography

of the sample as well as thermal and thermoelectric properties. We will describe the main parts of the SThM setup in the following.

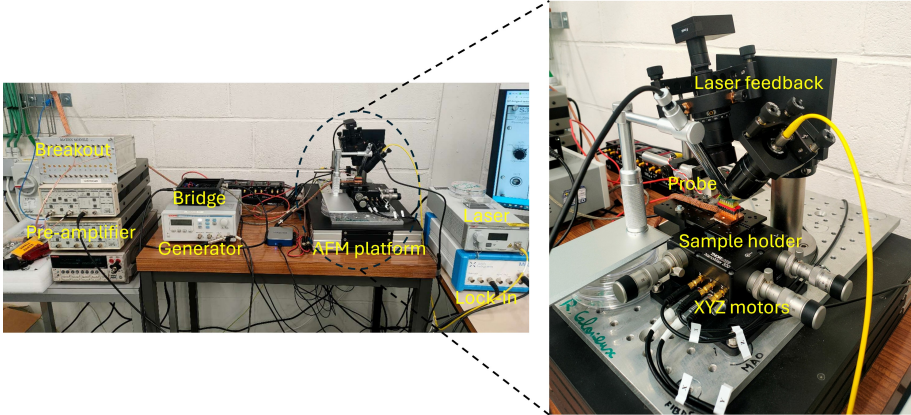


Figure 3.1: Optical images of the assembled SThM setup.

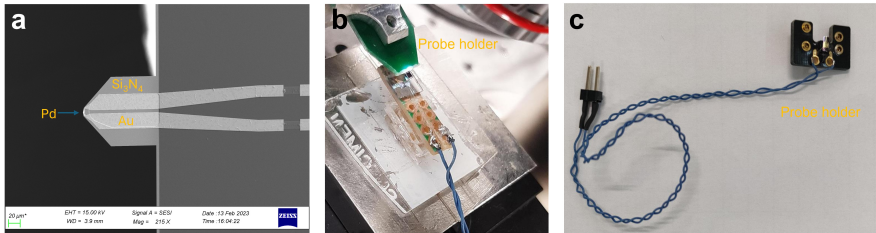


Figure 3.2: (a) SEM image of the KNT-SThM-2an probe. Optical images of the SThM probe holders for (b) the Thorlabs AFM and (c) the Bruker AFM.

AFM platform: The Thorlabs AFM consists of two main components: the controller and the scan head. The piezo-based controller, located beneath the sample holder, enables precise positioning and works as an XYZ scanner. It can be adjusted manually or driven electrically. A standard AFM feedback loop is employed to maintain

a constant force between the sample and the probe. The scan head can be adjusted manually to the right position for laser alignment and will be fixed during the scanning. A magnetic probe holder was used for easy attachment of the probe. This AFM requires few changes for SThM measurements: additional electrical systems for the SThM probe and sample. An EDU-AFM software is used to control the scanning process. In addition, we also use another AFM platform, the Bruker Dimension Icon, which offers a larger working area and scan range.

SThM probe: KNT-SThM-2an probes (Kelvin Nanotechnology) were used for this program. As shown in Figure 3.2a, this probe has two gold pads on the Si_3N_4 cantilever and a V-shaped Pd sensor at the tip apex. The tip has a radius of 50 nm, a spring constant of 0.4 N/m and a high temperature resolution of 0.1 K. The probe resistance is 300–350 ohms and the applied maximum current is 2.5 mA. Specialized cantilever holders are required for SThM probe. Figure 3.2b shows our home-made holder for Thorlabs AFM. The SThM probe was glued on a PCB with two copper or gold contacts. Figure 3.2c shows the standard cantilever for Bruker AFM through wire bonding to the gold contacts.

Wheatstone bridge: An additional electrical system is needed for SThM probe to precisely monitor its resistance variation. A customized SThM box with a Wheatstone bridge was fabricated based on a design from the group of prof. Oleg Kolosov in Lancaster University. Traditionally, a simplified Wheatstone bridge uses three fixed resistors and one tunable resistor. In SThM setup, the resistive probe is part of a resistor bridge (Figure 3.3a), which allows the detection of the small resistance change. Both DC and AC measurements are possible. Combined with the lock-in technique, AC measurement can be more sensitive with a lower drift and smaller uncertainties and therefore improve the signal-to-noise ratio. However, periodical probe heating driven by the AC current leads to periodical probe bending, which affects the mechanical stability of the probe. DC measurement can enhance the mechanical stability

of the tip-sample system but the sensitivity to the SThM signal changes is relatively low because of the limited DC current applied to the probe (less than 2.5 mA) [138]. Therefore, a combination of AC+DC bias was used to drive the probe. The DC part provides the self-heating while the AC part uses for detecting the SThM signal changes. Considering the parasitic capacitance from the cables in AC measurement, our bridge (Figure 3.3b) uses two variable resistors (R_2 for coarse tuning and R_3 for fine tuning) and two variable capacitors (C_1 and C_2) for balancing during standard operations. Before the measurement, we need to balance the bridge. The variable resistors and capacitors are adjusted until the output voltage is as close to zero as possible (experimentally less than 10 μ V). Any small change in the probe resistance then causes an imbalance in the bridge, resulting in a corresponding voltage output. Considering the SThM signal output is usually a weak signal, SThM box also includes an ultra-low noise amplifier (Figure 3.3b) to amplify the signal and improve signal-to-noise ratio. The optical image of the SThM box is shown in Figure A.2, and we will provide detailed usage instructions in Appendix A.

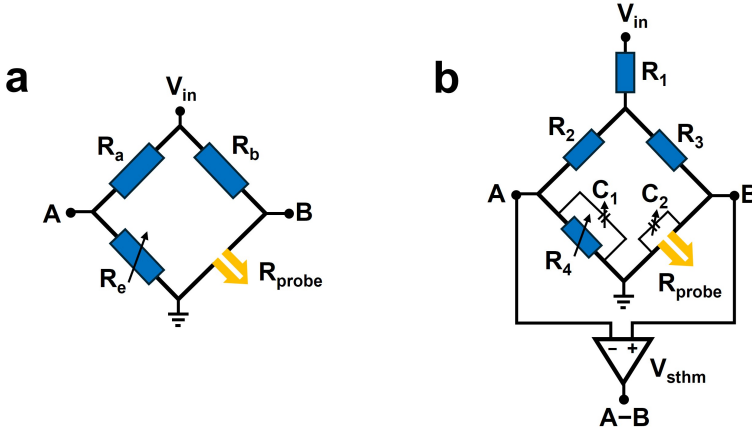


Figure 3.3: (a) Typical Wheatstone bridge for the SThM probe. R_a and R_b are the fixed resistors and R_e is the variable resistor to balance the bridge. The bridge output is the voltage between the A and B. (b) Our home-made Wheatstone bridge, two capacitors are used to balance the parasitic capacitance in AC measurement. A low-noise amplifier is used to improve the noise-to-signal ratio of the bridge output.

SThM measurements were performed by an AFM platform with a Kelvin SThM probe at an ambient environment. Figure 3.4 displays the schematic of the electrical circuit for real thermal and thermoelectric measurements. For thermal measurements, a combination of AC+DC is used. The bridge is first balanced, and then the function generator creates a dual AC and DC sinusoidal signal and sends it to the balanced SThM box. The probe is heated up and scans over the sample, the thermal resistance changes between the tip and the sample can be detected by the SThM box. The resulting SThM signal from the box then goes into the lock-in amplifier and obtains the recordable thermal signal at a specific reference frequency. For thermoelectric measurement, the device is electrically contacted with two electrodes. When the

probe is scanned over the sample, the global voltage drop between the two electrodes is measured with a pre-amplifier and then fed into the lock-in amplifier. In detail, the probe was heated up by applying a 2 V AC voltage at frequency of 91 kHz with a 2 V DC offset for thermal conductance measurement. The SThM signal is recorded from the bridge and then processed with lock-in amplifier at 91 kHz. Both AC (2ω) and DC measurements can be used for thermoelectric mapping. For DC measurements, the tip with a excess temperature ΔT (heated by 2 V AC at 91 kHz + 2 V DC) was scanned over the sample, DC thermovoltage V_{th} signal induced by the hot tip was processed with the low-noise preamplifier (SR560) and then recorded by SPM controller for data acquisition. For AC measurements, a low-frequency AC voltage (3 V at 57 Hz) was applied to SThM probe and the second harmonic signal $V_{2\omega}$ and phase were demodulated and recorded by a lock-in amplifier. This thermovoltage measurement method does not require an electrical contact between the tip and the sample, which can effectively reduce the measurement uncertainty and errors.

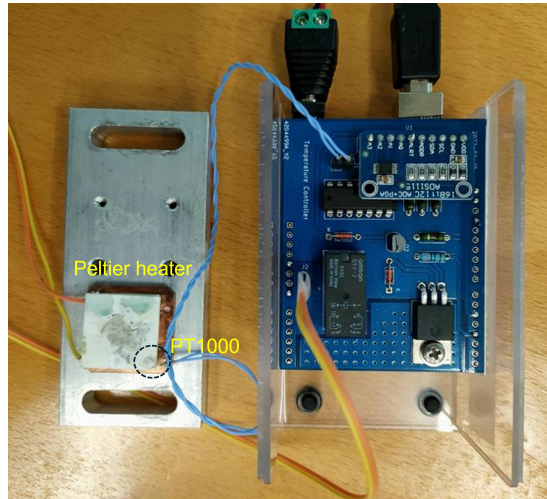


Figure 3.5: Optical image of the home-made temperature controller.

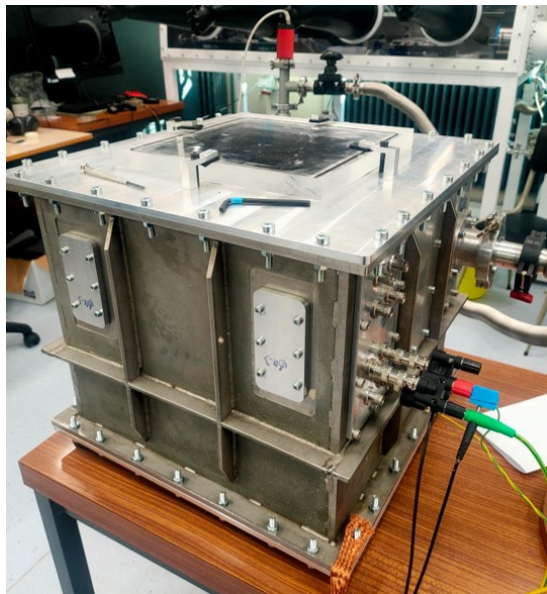


Figure 3.6: Optical image of the home-made vacuum chamber.

Vacuum SThM: SThM setup is capable of operating in both air and vacuum environments. Although all measurements of this project were performed in ambient environment, we have designed a vacuum chamber to support future development and functionalization of the SThM system. The Thorlabs can be placed in a customized vacuum chamber (Figure 3.6) which can reach a vacuum level below 10^{-2} mbar. In such conditions, the thermal conductivity of air is close to zero, effectively removing the air conduction, and greatly reducing the water meniscus between the tip and the sample. The vacuum chamber has various feedthroughs on the sides, which can be customized as needed for different experiments to allow transmission and measurement of multiple signals. A glass window on the top facilitates the installation, placement, and observation of the sample and probe. As mentioned in chapter 2, the doped silicon probe should be used under vacuum conditions for quantitative measurements at high resolution. This probe is different from the thermoresistive probe that the sensing/heating part is integrated at the end of the tip. The sample is separated from the sensing/heating area by the sharp conical tip (around $5\text{ }\mu\text{m}$ high) which has a very high thermal resistance. When using the doped silicon probe in air, this high resistance causes the heat to dissipate into the surrounding environment rather than being confined to the region below the apex. Therefore, the effective probed volume is much larger than the actual physical contact area just below the tip. With the vacuum chamber, we can conveniently use various SThM probes to achieve high-resolution measurements by minimizing the thermal transfer through the air and water meniscus. Furthermore, the designed Peltier temperature controller also can be used for controlling the sample temperature and probe calibration in vacuum.

3.2 SThM calibration

Before quantifying a tip-sample system using a thermal transport model, it is necessary to calibrate the probe before the measurement. Since we used the thermoresistive probes in an ambient environment, the first step of the probe calibration is temperature calibration. Out of contact calibrations are performed in air. We first determine the relationship between the probe electrical resistance (R_{probe}) and the temperature, specifically by identifying the TCR (α) of the probe. In this case, the probe is heated at different bath temperatures using a calibrated heater, we then measured the resistance of the probe by applying various powers to it. In the end, we measured the R_{probe} as a function of the temperature for each applied power. R_0 and α of the probe can be calculated from the calibration curve by this equation: $R_{\text{probe}}(T) = R_0 (1 + \alpha(T - T_0))$. Figure 3.7 shows the temperature calibration curves for the SThM probe used in this thesis. Although the baseline temperature T_0 of the probe varies due to the self-heating of the probe under the different applied powers, all these curves have the same slope. This indicates that the TCR of the probe remains constant and is not affected by the applied power. The slope of the curve corresponds to the product of R_0 and α . The mean value of the slope from all the calibration curves was used in this work, yielding a value of $(5.0 \pm 0.2) \text{ K } \Omega^{-1}$.

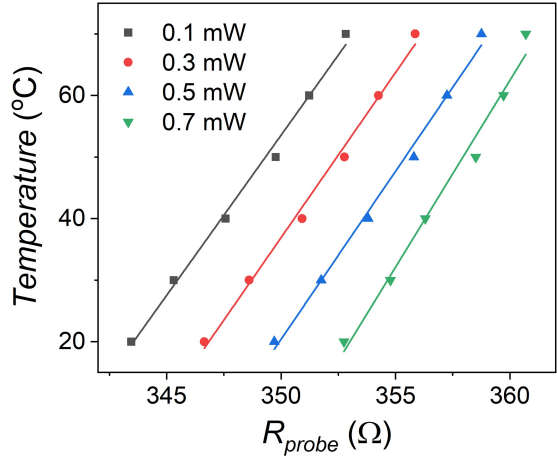


Figure 3.7: Temperature calibration of the SThM probe, showing the probe resistance as a function of the bath temperature at different applied powers.

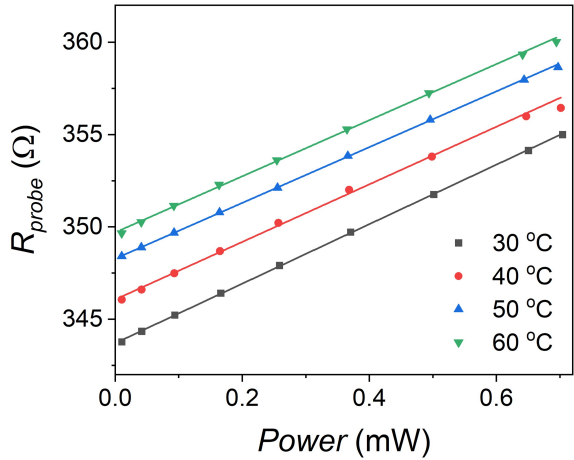


Figure 3.8: Electrical calibration of the SThM probe, showing the probe resistance as a function of the applied power to the tip at different bath temperatures.

The second step is the electrical calibration. In this calibration, the probe is heated up by Joule effect with a DC current and we measure the R_{probe} as a function of the applied power under the different temperatures. As shown in Figure 3.8, the R_{probe} linearly increases as different powers (from 0 to 0.7 mW) are applied to the probe. All these curves are parallel under different temperatures. We extracted the average slope of the curves and gave a value of $15.5 \Omega \text{ mW}^{-1}$.

In the end, combined with these two calibrations, we can convert the R_{probe} into the mean temperature rise of the Pd heater of the probe and obtain the relationship between the applied power (P) and the temperature rise of the probe (ΔT): $\Delta T \text{ (K)} = 85 \cdot P \text{ (mW)}$. The thermal conductance of the probe G_p can be calculated by equation $G_p = \frac{P_{\text{applied}}}{\Delta T} = 1.2 \times 10^{-5} \text{ W} \cdot \text{K}^{-1}$.

3.3 Analytical model of the SThM measurement

We first did out of contact calibration of the probe. The probe is far away from the sample surface. The Wheatstone bridge is balanced. The SThM signal output is below $100 \mu\text{V}$ with 100 mV applied to the probe. In real measurements, the probe is in contact with the sample. The variation of the SThM signal (V as a voltage) is recorded when the tip is scanning over the sample. The SThM signal corresponds to the heat transport from the probe to the sample, resulting in a temperature decrease of the probe and a local temperature rise of the sample. A typical approach-retraction curve of the SThM probe in ambient condition is shown in Figure 3.9. The SThM signal is recorded from the bridge as the probe approaches to the sample surface and then retracts. The SThM signal is proportional to the temperature rise of the probe heater. When the probe gradually approaches the sample surface, the SThM signal also decreases due

to the heat transfer from the air conduction and the radiation to the sample. As the probe is in contact with the sample surface, the solid-solid heat conduction is established, a sharp drop of the SThM signal (from V_{nc} to V_c) is observed because of additional heat transport through the R_{th} channel. Beyond the contact point, a small variation in the SThM signal can still be observed. This variation may result from slight changes in the contact area resulting from the increasing contact force. The same behavior was also observed in measurements conducted under vacuum conditions [85]. In addition, we observed that the approach and retract curves do not overlap, because the adhesion force between the tip and sample surface during the retraction process require an increased force to rupture the contact. Specially in air, this adhesion force becomes higher due to the water meniscus. From the SThM signal drop, we extract the SThM response $\frac{dV}{V} = \frac{V_{nc}-V_c}{V_{nc}}$ and used this value to calculate the tip-sample thermal resistance R_{th} for all thermal maps.

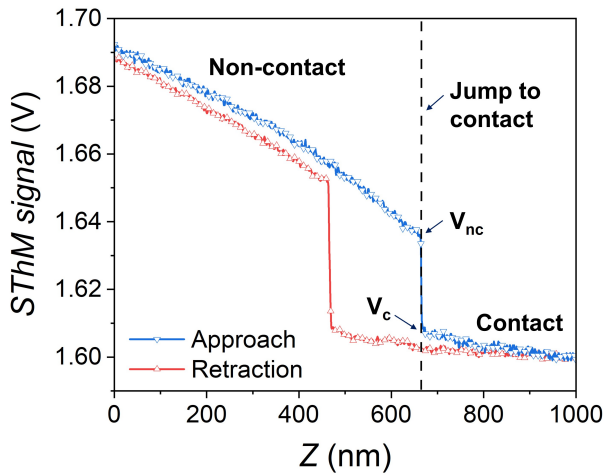


Figure 3.9: Tip-sample approach (blue) and retraction (red) curves for thermal response recorded on a MXene flake on SiO_2 substrate during the probe calibration.

In probe calibration, we extracted the relationship between the excess temperature with respect to the probe base temperature and the applied power. This excess temperature (ΔT) then is proportional to the SThM output voltage (V_{sthm}), by a calibration factor β :

$$\Delta T = \beta V_{\text{sthm}} \quad (3.1)$$

Figure 3.10 shows a simplified heat transport model of the probe and sample system, which was developed based on the previous works [85, 139]. When the tip is out of contact, the heat transfer channel is through the cantilever. So we obtain $\Delta T_{\text{nc}} = \beta V_{\text{nc}} = P \times R_{\text{p}}$, where P is the applied power and R_{p} is the thermal resistance of the cantilever. From the calibration curves, we measure $R_{\text{p}} = 8.5 \times 10^4 \text{ K W}^{-1}$.

When the probe is in contact with the sample surface, a new heat transfer channel R_{th} is established, and the heat dissipates from the tip to the sample. We assume all heat sinks (the probe base and the sample) have the same temperature: $T_{\text{m}} = T_{\text{s}} = T_0$. We obtain:

$$\Delta T_{\text{c}} = P \times R_{\text{tot}} = P \times \frac{R_{\text{p}} R_{\text{th}}}{R_{\text{p}} + R_{\text{th}}} \quad (3.2)$$

where $R_{\text{tot}} = R_{\text{p}} + R_{\text{th}}$ and R_{th} is the thermal resistance of the tip-sample heat transfer channel. R_{th} includes three components in series: the thermal resistance of the sharp tip R_{tip} , the interface resistance of between the tip apex and the sample surface R_{int} , and the spreading resistance of the sample R_{spr} . A model is needed to calculate the R_{th} . Based on the previous work [140], we obtain the normalized temperature change between non-contact and in contact and it can be described by the following expression:

$$\frac{\Delta T_{\text{nc}} - \Delta T_{\text{c}}}{\Delta T_{\text{nc}}} = \frac{V_{\text{nc}} - V_{\text{c}}}{V_{\text{nc}}} = \frac{R_{\text{p}} - R_{\text{tot}}}{R_{\text{p}}} = \frac{R_{\text{p}}}{R_{\text{p}} + R_{\text{th}}} \quad (3.3)$$

As we can see, the SThM response dV/V is only dependent on the R_p and R_{th} . The measured thermal resistance R_{th} can be directly obtained from the probe calibration and approach-retraction curves.

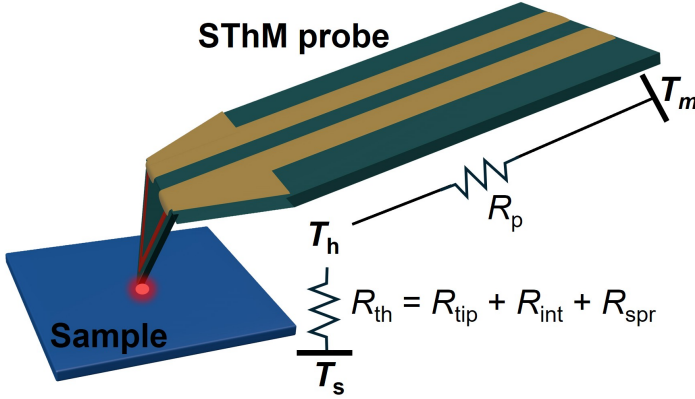


Figure 3.10: Schematic diagram of the SThM system. The probe is at the temperature of T_h thermally connected to the microscope at the temperature of T_m through the probe thermal resistance R_p . The sample temperature is T_s . The heat transfer from the tip to sample is through the thermal resistance R_{th} which includes the tip, interface and spreading thermal resistances.

3.4 MXenes synthesis and exfoliation

3.4.1 Mo_2CT_x synthesis and characterization

Mo_2CT_x MXene used in this chapter was synthesized by selectively etching Ga from $\text{Mo}_2\text{Ga}_2\text{C}$ from a mixed solution of ammonium fluoride (NH_4F) and hydrochloric acid (HCl) based on the reported method [141]. Figure 3.11 shows the preparation process of few-layers Mo_2CT_x MXene. In detail, 200 mg $\text{Mo}_2\text{Ga}_2\text{C}$ powder

(purchased from 2D semiconductors Inc.) was added to a 10 ml Teflon-lined autoclave, which is composed of 400 mg NH_4F and 4 ml 6 M HCl . The autoclave was sealed and kept at the temperature of 140 °C for 24 h. After the reaction, the autoclave was cooled down to room temperature naturally and got the Mo_2CT_x mixture. This mixture was centrifuged (5000 rpm) for 5 min and washed with DI water until the pH value of the upper solution is 6.

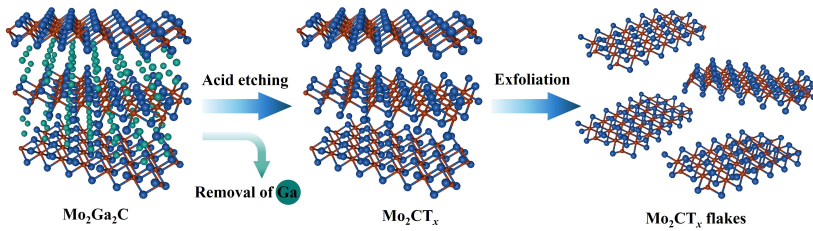


Figure 3.11: Schematic diagram of the synthesis and exfoliation processes of the Mo_2CT_x MXene flakes.

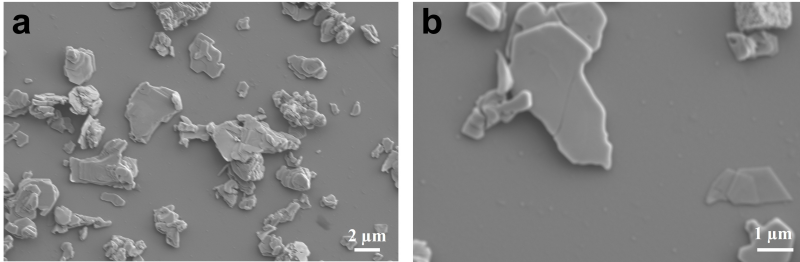


Figure 3.12: SEM images of the exfoliated Mo_2CT_x flakes on SiO_2 substrate.

For the liquid-phase exfoliation process, the Mo_2CT_x sediment was dispersed in DI water or ethanol again. We can separate the layers of Mo_2CT_x via ultrasound treatment for 30 min. Then the resulting mixture is centrifuged (10000 rpm) for 10 min. The dark

upper solution, which contains a high concentration of few-layer Mo_2CT_x flakes, was carefully collected, while the large multilayer flakes or unetched bulk materials remained in the sediment. After drying the upper solution, we also can obtain the Mo_2CT_x powder. We also attempted to exfoliate the flakes using mechanical methods, such as Scotch tape. However, the results were not satisfactory, primarily due to the strong interlayer interactions in MXenes and the presence of residual metallic bonding from incomplete etching.

The microstructure morphology of Mo_2CT_x flakes was characterized by a scanning electron microscope (SEM), as shown in Figure 3.12. The layered structure of the MXene multilayers is clearly visible after the etching process. The flake sizes are typically on the order of a few micrometers. However, thinner flakes tend to be significantly smaller due to fragmentation caused by the sonication treatment.

The Raman spectra of the few-layer Mo_2CT_x flake is shown in Figure 3.13. We measured Raman spectra for both Mo_2CT_x and the corresponding background. The background was then subtracted to remove contributions from the substrate and other environmental signals. According to the previous Raman studies on Mo_2CT_x [142, 143], the peak at 122 cm^{-1} is assigned to the E_{2g} group vibration which corresponds to in-plane modes of Mo and C atoms, while the peaks at 232 cm^{-1} is attributed to A_{1g} group vibration, which reflects the out-of-plane vibration of Mo and C atoms. The peak at 847 cm^{-1} is resulted from the resonance Raman enhancement for MoO_3 nanoparticles [142]. The Raman signal is weak when the flake thickness is reduced.

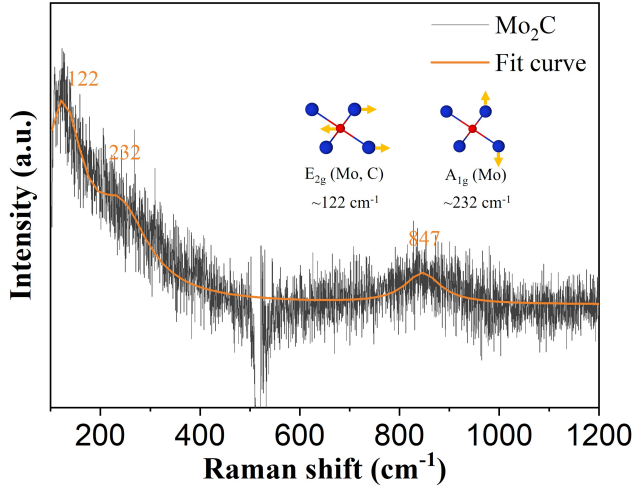


Figure 3.13: Raman spectrum of the Mo_2CT_x flake under the 514 nm laser.

3.4.2 $\text{Ti}_3\text{C}_2\text{T}_x$ and V_2CT_x synthesis and characterization

The two other MXenes used in this study are produced by our collaborators, Prof. Gogotsi group in Drexel University. They offer the advantage of easy preparation of monolayer to few-layer flakes with large lateral sizes exceeding $10\text{ }\mu\text{m}$. Additionally, a milder synthesis process was used for both MXenes, resulting in higher-quality flakes with fewer defects than Mo_2CT_x . Compared to Ga-based MAX phase, Al-based MAX phases are much easier to etch and exfoliate. Especially for $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, several methods [144, 145] have been investigated and optimized to synthesize the large-size MXene flakes in our collaborator's group. These flakes enable us to transfer them using a stamping setup and to make contacts for further thermal and thermoelectric measurements. Figure 3.14 shows the optical images of $\text{Ti}_3\text{C}_2\text{T}_x$ and V_2CT_x flakes on SiO_2 wafer, with the flake size over $5\text{ }\mu\text{m}$ and flake thickness less than

10 nm. The detailed synthesis process will be introduced in chapter 4 and 5.

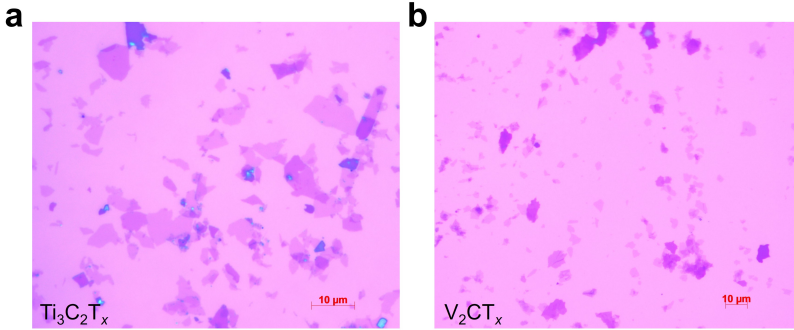


Figure 3.14: Optical images of the (a) $\text{Ti}_3\text{C}_2\text{T}_x$ and (b) V_2CT_x MXene on SiO_2 substrate.

3.5 Device fabrication

MXene flakes should be isolated onto a substrate before the measurements. A Si/ SiO_2 wafer with a 290 nm-thick oxide layer was used for all device fabrication in this work, as it is often used for 2D materials and enables easy flake identification under an optical microscope. For SThM thermal transport measurements of MXenes, electrical contacts are not required. A simple method involves drop-coating the MXene solution on the Si/ SiO_2 substrate and dried in an oven. The monolayer and few-layer flakes were deposited on the wafer and then we can directly study the thickness-dependent thermal transport using SThM technique. Optical images of the transferred flakes on wafer with different thicknesses are shown in Figure 3.14.

However, for electrical and thermoelectric measurements, electrical contacts on the flake are needed. In this project, we used two methods to make contacts on MXene flakes. One is pre-patterned metal contacts [Ti (3 nm)/Au (30 nm)] using the E-Beam lithogra-

phy and metal evaporation deposition, the other is directly deposited indium needles as contacts.

3.5.1 EBL and metal evaporation deposition

The pre-patterned device involved the oxygen plasma, EBL and metal evaporation deposition in the fabrication process. The whole process is working in a clean environment (Cleanroom on Winfab platform at UCLouvain). Dust or dirt are often larger than the device structures and can disrupt the fabrication process. The purchased 3-inch wafer is first divided into 1 cm² pieces and then is thoroughly cleaned. The diced chips are sonicated in acetone for 10 min and subsequently washed with isopropanol (IPA) and DI water. After drying with a nitrogen flow, the chips are further treated with oxygen plasma to remove any possible surface contamination. The chips are prepared for the EBL patterning. In a typical process, an E-beam resist is spin-coated onto the chip. To ensure a uniform coating, this is done in a spin-coating machine where the wafer is mounted on a rotating stage using a vacuum chuck. The thickness of the coating film can be controlled by the composition and concentration of the resist as well as the spinning speed. In our case, we used double positive resist layers (Methacrylic acid/Poly(methyl methacrylate) (MAA/PMMA)). After drop-coating the first layer of 9% MAA resist onto the wafer, it is spun at 5000 rpm for 1 minute to achieve the desired thickness (Figure 3.15a). The wafer is then baked at 180 °C for 15 minutes, a temperature above the glass transition point of the resist. The baking step helps to uniformize the film and evaporate any residual solvent in the resist. For the second layer (Figure 3.15b), a 2% PMMA resist is used, followed by the same spin-coating and baking process as used for the first layer. Now the wafer is ready for EBL exposure.

Depending on the application and patterning process, either a positive or negative resist can be chosen. In this project, we aim to deposit metal layers, so a positive resist is used. The EBL machine

works by focusing a high-energy electron beam in a user-defined pattern on the resist. The regions exposed by the EBL will be removed during development, allowing metal deposition only in the desired areas. For the writing of the contacts, EBL was performed on the Raith Pioneer II. The machine was operated at 10 kV and a beam aperture of 30 μm with a beam current of 0.9 nA. The exposure dose is an important parameter and needs to be carefully adjusted to achieve the desired pattern resolution and edge sharpness. A clearing dose of 110 $\mu\text{C cm}^{-2}$ is used for the PMMA resist. As shown in Figure 3.15c, the electron beam interacts differently with the two layers of the double-layer resist: the top layer is PMMA, and the bottom layer is a copolymer of MAA. Due to electron backscattering from the SiO_2 substrate, the bottom MAA layer experiences more exposure and creates an undercut during development (Figure 3.15d). This undercut facilitates clean liftoff in metal deposition.

After e-beam exposure, the wafer is washed by the developer to dissolve and remove the cleaved polymer chains in the exposed regions of the resist. Typically, the wafer is developed by immersing it in IPA/MIBK (IPA: methyl isobutyl ketone in a 3:1 ratio) for 30 seconds, followed by washing in IPA for another 30 seconds to stop the developing process. We can then check the developed pattern under an optical microscope. The next step is to deposit the desired metal layer onto the patterned resist using a thermal evaporator (Figure 3.15e). For Au contacts, a few nanometers of Ti layer are first deposited to serve as an adhesion layer between the Au and the substrate. This is followed by the deposition of an Au layer approximately 30-50 nm thick. The thickness of the Au layer should be sufficient to support wire bonding on the Au pads later. After the metal deposition, the lift-off process is performed by washing the wafer in acetone to dissolve the remaining resist (Figure 3.15f). Finally, the pre-patterned metal layers are deposited on the wafer.

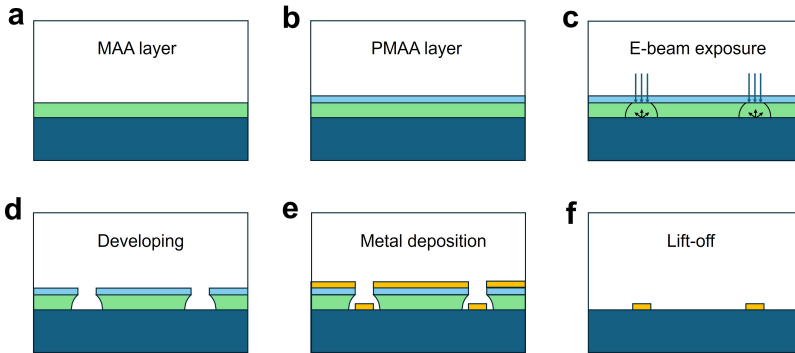


Figure 3.15: Schematic diagram of the pre-patterned metal deposition. (a) Coating the first MAA resist on SiO_2 substrate. (b) Coating the second layer of PMMA resist. (c) E-beam exposure, showing the electron backscattering from the substrate. (d) Developing the exposed resist with an undercut. (e) Deposition of the metal layer using a thermal evaporator. (f) Lift-off process to remove the resist layers and leave the final metal structure on the substrate.

3.5.2 Transfer methods for MXene flakes

Since MXene flakes are exfoliated in a liquid medium (DI water in this project), the drop-coating method can transfer flakes onto the wafer, but it is a random process that does not allow control over flake positioning. In order to precisely transfer MXene single flakes on the pre-patterned devices and fabricate MXene homostructures or heterostructures (*e.g.*, graphene-MXene heterojunction), we employed a polymer-assisted transfer method using a home-built stamping setup. A Poly(propylene carbonate)/Polydimethylsiloxane (PPC/PDMS) stack was used in our experiment, where a thin PPC film ($<1\mu\text{m}$) was covered on the top of the PDMS stack. The MXene solution was then drop-casted on the PPC/PDMS stack and dried with a nitrogen flow (Figure 3.16a). The single flakes were adhered to the surface of PPC film and identified by opti-

cal microscopy. The glass slide was then placed on the transfer stage. After the alignment on pre-patterned device, the MXene flake was stamping on top of the gold contacts and then heated up the temperature to 80 °C (above the glass transition temperature of the PPC), because the adhesion between MXene flake and PPC decreases above this temperature. The MXene flake was slowly released onto the pre-patterned device followed by a cleaning step in acetone, isopropanol and DI water to remove the polymer residues (Figure 3.16b). Compared to a PDMS-only stack, there are some advantages by using PPC thin film: 1) Because of the hydrophilic nature of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, achieving flat adhesion directly on PDMS is challenging. The polar groups in PPC improve the adhesion of the flake, which is critical for precise positioning and alignment on pre-patterned device; 2) The thin PPC layer facilitates the optical identification of MXene monolayers under a microscope; 3) PPC has less polymer residues than PDMS after the transfer process, resulting in a cleaner MXene surface.

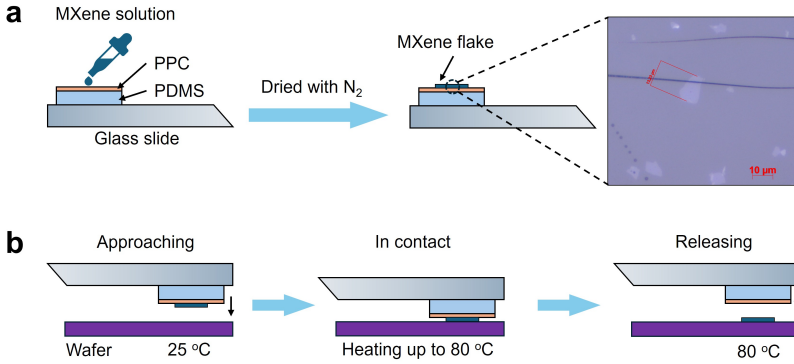


Figure 3.16: Schematic of the PPC/PDMS stamping method. (a) Step 1: MXene solution was drop-casted on PPC and dried with nitrogen. Optical image shows the flake on PPC surface. (b) Step 2: The PPC/PDMS stack containing the MXene flake placed on the transfer stage and approached to the pre-patterned device and then released at 80 °C.

For graphene, hBN is typically used to pick up the graphene exfoliated on the wafer [146]. We also attempted to use a thin hBN flake to pick up the MXene flake from the SiO_2 substrate. However, it is difficult to pick up the MXene flake. This is likely due to the relatively weak van der Waals interaction between hBN and the MXene surface, as well as the potential surface contamination (water molecule absorption) or oxidation of MXene. It is true that other flakes than hBN with stronger adhesion to MXene flakes could help to pick up the MXene flake. This will be explored in future work. In addition, picking up the MXene flake from the SiO_2 substrate using a PPC film also fails, because of the strong adhesion between the MXene flake and the substrate. To this end, we deposit the MXene flake directly onto the PPC film and subsequently transfer it onto the target substrate using a dry transfer technique. It is worth noting that the MXene flake is fragile and prone to breaking during the transfer process. Therefore, it is crucial to approach and

release the PPC/PDMS stack very slowly and carefully to minimize mechanical stress on the flake.

3.5.3 Indium needle contacts

The indium needle soldering technique [147] is a one of the lithography-free contacting techniques, which enables directly to make electrical contacts on MXene flakes. It provides a simple and effective method for making submicron-sized, Ohmic contacts to 2D flakes without contaminating the sample. Figure 3.17 presents the main parts of the soldering setup. It operates at the stamping setup. Similar to the MXene transfer process, a tungsten tip is glued at the end of a glass slide. The sample is placed on the holder with a small indium bread nearby. The temperature of the holder is heating up to around 170 °C (a bit above the melting point of the indium). It is worth noting that temperature is a crucial parameter for forming a sharp and continuous needle. The tungsten is then inserted into the molten bead using the XYZ micromanipulators and gradually pushed out to form an indium needle. The indium needle is inspected under an optical microscope. It is then positioned and aligned with the MXene flakes, and finally successfully transferred onto the flakes. Repeating the above process to make the desired contacts. Wire bonding can also be performed directly on the indium needles.

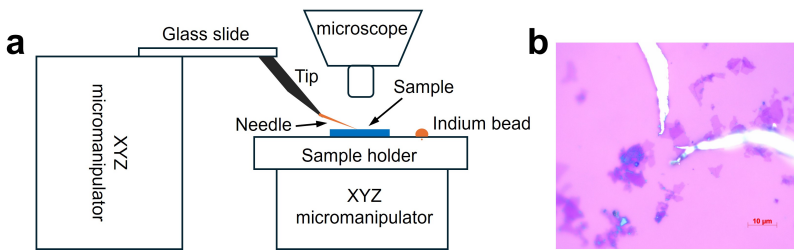


Figure 3.17: (a) Schematic of making the indium needle contact on the sample using a stamping setup. (b) Optical image of the MXene flakes contacted with two indium contacts.

Chapter 4

Thermal transport of single $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes

The high electrical conductivity and good chemical stability of MXenes offer hopes for their use in many applications, such as wearable electronics, energy storage, or electromagnetic interference shielding. While their optical, electronic and electrochemical properties have been widely studied, the information on thermal properties of MXenes is scarce. In this chapter, we investigate the heat transport properties of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene single flakes using scanning thermal microscopy and find exceptionally low anisotropic thermal conductivities within the $\text{Ti}_3\text{C}_2\text{T}_x$ flakes, leading to an effective thermal conductivity of $0.78 \pm 0.21 \text{ W m}^{-1} \text{ K}^{-1}$. This observation is in stark contrast to the predictions of the Wiedemann-Franz law, as the estimated Lorenz number is only 0.25 of the classical value. Due to the combination of low thermal conductivity and low emissivity of $\text{Ti}_3\text{C}_2\text{T}_x$, the heat loss from it is two orders of magnitude smaller than that from common metals. Our study explores the heat transport mechanisms of MXenes and highlights a promising approach for developing thermal insulation, two-dimensional thermoelectric, or infrared stealth materials.

4.1 Introduction

Materials with low thermal conductivity are of utmost importance for a plethora of applications ranging from thermal insulation, to heat shields, and stealth materials, as well as to thermoelectrics [148]. In this context, 2D materials have gained increasing attention since they can possess very low lattice thermal conductivities, because of their two-dimensional crystal structure and phonon-boundary scattering. For example, WSe_2 [149], gallium phosphide (GaP) [150] and indium selenide (InSe) [86] reached low values of $0.048 \text{ W m}^{-1} \text{ K}^{-1}$, $1.52 \text{ W m}^{-1} \text{ K}^{-1}$ and $28.7 \text{ W m}^{-1} \text{ K}^{-1}$, respectively, which were explained by the strong phonon anharmonicity and boundary scattering. However, these materials often have a low electrical conductivity, making them impractical for use in thermoelectric heat engines. This kind of green energy harvester can generate electricity from the heat with an efficiency proportional to the figure of merit $ZT = \frac{\sigma S^2 T}{\kappa}$, where σ , S and κ are the electrical conductivity, the Seebeck coefficient, and the total thermal conductivity, respectively. Therefore, materials with *low* thermal conductivity and *high* electrical conductivity are desired, a property that is inherently difficult to achieve: in most electrically conductive solids, charge carriers also transport heat. Indeed, the electronic thermal conductivity (κ_e) is related to the electrical conductivity via the Wiedemann-Franz (WF) law. It states that the ratio of κ_e to σ at a given temperature (T) is a constant called the Lorenz number (L_0):

$$L = \frac{\kappa_e}{\sigma T} \equiv L_0 = 2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}. \quad (4.1)$$

In recent years, it has been experimentally demonstrated that this *fundamental* law can be violated in some materials like graphene [56], VO_2 [151] or in quantum-confined 0D systems [57]. A key ingredient for this violation appears to be strong correlations of quasiparticles, such as strong electron-phonon coupling [56]. To this end, a large family of 2D materials, transition metal carbides and

nitrides (MXenes) [4], might be able to demonstrate this violation because some MXenes like $\text{Ti}_3\text{C}_2\text{T}_x$ have a highly tunable metallic-like conductivity of 5000 to over 20000 S cm^{-1} [23] combined with strong electron-phonon interactions [35, 36, 152]. However, while their electronic properties have been widely investigated, experimental studies on their thermal transport properties remain lacking, especially on the intrinsic thermal conductivity of isolated single flakes.

In this chapter, we present local thermal transport measurements on $\text{Ti}_3\text{C}_2\text{T}_x$ MXene single flakes by using scanning thermal microscopy (SThM) at room temperature. By measuring the thermal conductance variation with varying flake thickness, we extracted an ultra-low thermal conductivity of $0.78 \text{ W m}^{-1} \text{ K}^{-1}$. It coexists with a high electrical conductivity of $>4430 \text{ S cm}^{-1}$ which leads to a strong violation of the WF law in $\text{Ti}_3\text{C}_2\text{T}_x$ single flakes, with $L = 0.25L_0$. Therefore, our work demonstrates that MXenes provide highly promising 2D materials for ultra-thin heat insulation or thermoelectric applications.

4.2 Synthesis and characterization of $\text{Ti}_3\text{C}_2\text{T}_x$ flakes

$\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes were synthesized following a well-established process [153] by the group of Prof. Gogotsi. In detail, $\text{Ti}_3\text{C}_2\text{T}_x$ was etched from Carbon Ukraine Ti_3AlC_2 MAX phase. The etchant was prepared by mixing 6 mL deionized water, 2 mL hydrofluoric acid (51 wt.% aq. Thermo Fisher Scientific), and 12 mL hydrochloric acid (38 wt.% aq. Thermo Fisher Scientific). 1 g Ti_3AlC_2 was then etched for 24 hours at 35°C and 300 rpm for the stir bar. After etching out the Al, the acid was washed out of the multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ through 8 cycles of centrifugation at 3500 rpm for 3 min per cycle. Once the solution was pH neutral, H_2O was added to make a 20 mL solution,

and 0.424 g LiCl was added to make a 0.5 M concentration of Li^+ ions, which were then intercalated into the $Ti_3C_2T_x$ by mixing for 24 hours at 35 °C and 300 rpm. After intercalation, the monolayer and few-layer MXene flakes were isolated through repeated centrifugation and skimming, as only the single flakes remained suspended for collection after centrifugation. Centrifugation conditions were 10 min and 3500 rpm to remove LiCl and repeated until supernatant was no longer clear, with subsequent increases in cycle time for single-layer MXene supernatant collection. About 10-12 cycles were performed, and then the predominantly single-layer $Ti_3C_2T_x$ dispersion was concentrated through centrifugation at 10000 rpm for 20 min.

Samples of $Ti_3C_2T_x$ isolated flakes were obtained by drop-casting MXene aqueous dispersion onto a Si/SiO₂ (290 nm-thick SiO₂) substrate, followed by washing with slowly flowing deionized water and naturally dried under a flow of nitrogen gas. The wafers were finally put in an oven at 60 °C to completely dry the flakes. Before deposition, the Si/SiO₂ wafer was ultrasonically cleaned in acetone and then deionized water for 10 min to ensure the cleanliness of the surface. We obtained lots of single MXene flakes with different thicknesses within the drop-cast area. The indium needles were fabricated in $Ti_3C_2T_x$ single flake as electrical contact, which can achieve good ohmic contacts. The detailed fabrication procedure is described in chapter 3.

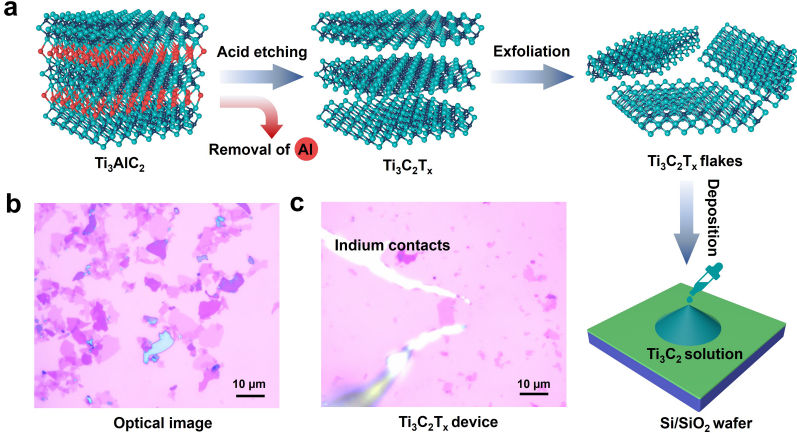


Figure 4.1: (a) Schematic of the preparation process of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene single flakes and devices. (b) Optical image of monolayer and few-layers $\text{Ti}_3\text{C}_2\text{T}_x$ flakes on SiO_2 substrate. (c) A two-terminal $\text{Ti}_3\text{C}_2\text{T}_x$ device of single flake contacted with two indium needles.

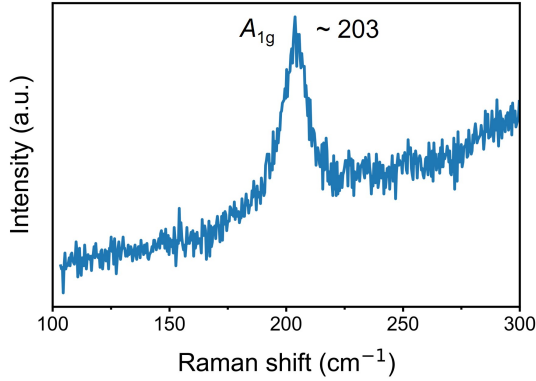


Figure 4.2: Raman spectrum of the monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ under the 514 nm laser.

Briefly, we first etched the aluminium layers of the MAX phase (Ti_3AlC_2) in acidic solution, followed by liquid exfoliation to prepare

a colloidal suspension of $\text{Ti}_3\text{C}_2\text{T}_x$ flakes in water (see Figure 4.1a). The detailed structure of $\text{Ti}_3\text{C}_2\text{T}_x$ has been characterized by the Gogotsi's group [154]. We further measured the Raman spectrum of a monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ with 514 nm excitation. As shown in Figure 4.2, we observed a characteristic Raman peak at approximately 203 cm^{-1} . This peak corresponds to the out-of-plane vibration mode A_{1g} (involving Ti, C, and T_x) and agrees with previous studies [36, 83]. Due to the strong Raman signal from SiO_2 substrate, peaks corresponding to the MXene sample at higher wavenumbers are not clearly visible in our measurements.

Isolated high-quality $\text{Ti}_3\text{C}_2\text{T}_x$ flakes with lateral sizes of 5 to $20\text{ }\mu\text{m}$ were obtained by drop-casting the dispersion on a Si/ SiO_2 wafer. Figure 4.1b shows an optical image of a typical deposit. From their optical contrast (in combination with atomic force microscopy (AFM), Figure 4.3b), the thickness of $\text{Ti}_3\text{C}_2\text{T}_x$ flakes can be obtained and flakes with thicknesses varying down to the monolayer limit ($\approx 1.8\text{ nm}$, Figure 4.3d) are identified. For electrical conductance measurements, we fabricated devices by nano-scale soldering of indium [132, 147] to the single flakes (Figure 4.1c).

4.3 Thermal transport in $\text{Ti}_3\text{C}_2\text{T}_x$ flakes

4.3.1 SThM measurements on $\text{Ti}_3\text{C}_2\text{T}_x$ devices

The measurement detail can be found in chapter 3. In brief, we first zeroed the Wheatstone bridge and heated the probe with applying $2\text{ V AC} + 2\text{ V DC}$. The probe was scanned over the sample area with contact mode, and the thermal response V_{SThM} was measured with lock-in amplifier (SRS830) pixel by pixel from the unbalanced bridge caused by the local thermal conductance changes of the sample. By monitoring V_{SThM} , we can create a thermal resistance map of the MXene sample. Finally, the amplified signals were recorded by scanning probe microscope controller for data acquisition using

commercial software. Topography and thermal maps of $Ti_3C_2T_x$ devices could be obtained simultaneously.

To investigate the thermal transport properties of isolated $Ti_3C_2T_x$ flakes with different thicknesses, from monolayer to tens of layers, we used ambient SThM at room temperature ($T_{room} = 293$ K). SThM is a contact mode atomic force microscopy technique in which microfabricated probe is equipped with a Pd electrical resistor on the cantilever and close to the tip apex (see Figure 4.3a). This resistor is used as a temperature sensor and local heater, and its resistance is measured using a custom-made Wheatstone bridge as we discussed in the chapter 3 [139, 140]. Then, the probe is brought into contact with the sample surface. When the mechanical contact occurs, a sharp drop of the probe temperature is observed due to the extra heat transfer opened at the tip apex. Finally, when the tip raster scans the sample surface, the probe temperature is mapped onto the sample topography allowing to calculate the heat flow into the sample and its thermal resistance.

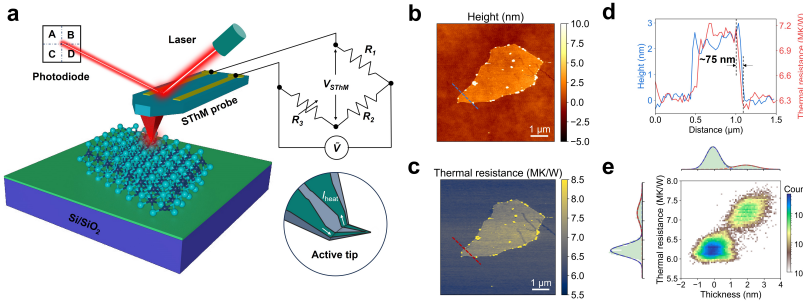


Figure 4.3: (a) Schematic of the SThM setup for measuring local thermal transport properties of $Ti_3C_2T_x$ flakes. The SThM probe can be used for temperature sensing (with a palladium circuit at the tip apex). Thermal transport signal is measured from Wheatstone bridge output. (b) Topography and (c) thermal resistance maps of monolayer $Ti_3C_2T_x$ on SiO_2 acquired in an ambient environment. (d) Height and thermal resistance curves along the dashed blue line in (b) and red line in (c). Vertical dashed lines are used to estimate the lateral thermal resolution and the tip radius of the SThM probe, which are 38 nm and 75 nm, respectively. (e) 2D histogram showing the relationship between thickness and thermal resistance of the entire image, mean values can be obtained from the Gaussian fit.

4.3.2 Conversion of SThM signal to thermal resistance

To convert the SThM signal to thermal resistance, we first need to calibrate the SThM probe and record the approach-retraction curve. The detailed calibration process can be found in chapter 3. We then extracted the SThM response $(V_{nc} - V_c)/V_{nc}$ and used this value to calculate the thermal resistance for all image pixels. In the end, we converted the SThM signal map (V_c) to the thermal resistance map (R_{th}) using the Equation 3.3. Figure 4.3b and 4.3c show a topography and thermal resistance map of a single layer $Ti_3C_2T_x$

flake simultaneously obtained using SThM. We observed a strong thermal resistance contrast between the $\text{Ti}_3\text{C}_2\text{T}_x$ monolayer and the SiO_2 substrate. The thermal resistance increases from 6.3 MK W^{-1} on bare SiO_2 to 7.1 MK W^{-1} on monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ flakes (see Figure 4.3d). It is worth to note that while such increased thermal resistance can point towards a lower thermal conductivity of $\text{Ti}_3\text{C}_2\text{T}_x$ compared to that of SiO_2 , there can be other factors playing a significant role in the apparent thermal transport: i) the thermal contact between the SThM probe and surface can be different for SiO_2 and $\text{Ti}_3\text{C}_2\text{T}_x$; ii) the newly formed interface between the monolayer and SiO_2 substrate can lead to enhanced phonon scattering and thus increased thermal resistance [85, 103]; iii) monolayer flake tends to present a thermal barrier, since its enhanced in-plane thermal spreading is poor when compared to the new interface resistance [103].

4.3.3 Dataset of SThM thermal maps on $\text{Ti}_3\text{C}_2\text{T}_x$ flakes

Generally, impurities and defects (such as wrinkles and bubbles) of $\text{Ti}_3\text{C}_2\text{T}_x$ can cause spatial variations in the local thermal conductance. The topography in Figure 4.4a shows some wrinkles along the edges, which correspond to the brighter areas in the obtained thermal resistance image (Figure 4.4b). We also obtained the 2D histogram image for few layers with different thicknesses (Figure 4.4c) by using the same method as for monolayer flakes. The data set also shows a good Gaussian distribution. We finally obtained seven thermal maps with various flake thicknesses and used as our data set to fit a thermal transport model for extracting the thermal conductivity of $\text{Ti}_3\text{C}_2\text{T}_x$ flake. To fit all measured data with a diffusive heat transport model described by Equation 2.10, we assume the R_{tip} and R_{int} are independent of the thickness of $\text{Ti}_3\text{C}_2\text{T}_x$. In detail, we divided the 2D histogram image into small bins and chose

the bins with the largest counts in each column as the fitting points. By fitting them to the experimental data R_{th} , we can estimate the k_i and k_c of $\text{Ti}_3\text{C}_2\text{T}_x$, as well as the R_{tip} and r_{int} with them as unknown fitting parameters. The fitting error was also estimated from the covariance matrix when reaching the best fit, we got only $\approx 1\%$ standard errors for k_i and k_c values.

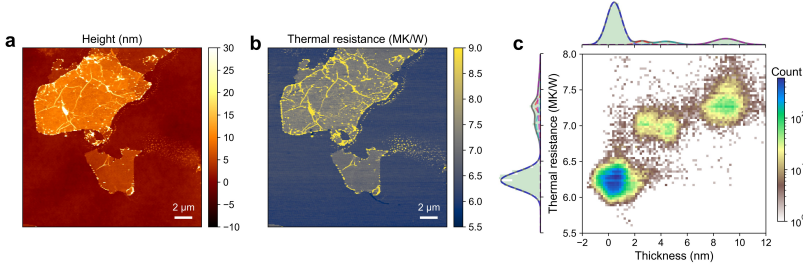


Figure 4.4: (a) Topography and (b) thermal resistance maps of a few layers $\text{Ti}_3\text{C}_2\text{T}_x$ on SiO_2 acquired under ambient environment. (c) 2D histogram profile showing the relationship between thickness and thermal resistance of the entire image and the Gaussian fit curves.

4.4 Extracting the thermal conductivity of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene

After conversion of the SThM signal to thermal resistance, another key parameter for extracting the thermal conductivity of $\text{Ti}_3\text{C}_2\text{T}_x$ is tip radius. The thermal lateral resolution and the tip radius can be estimated from the thermal resistance profile in the dark dashed line region (Figure 4.3d). We use the lateral distance of the thermal resistance changes when the tip moves from monolayer MXene to substrate. Taking half of the full width as the resolution criterion, thus the thermal lateral resolution and the tip radius are around 38 nm and 75 nm, respectively [85, 103]. After calibrating the probe,

we can use the diffusive thermal transport model described above to extract the thermal transport properties of $\text{Ti}_3\text{C}_2\text{T}_x$, including its thermal conductivity. We note that a constant tip-sample radius is assumed in our experiments. This assumption is generally valid when the same probe is used on the same material and the sample surface does not exhibit sharp corrugations.

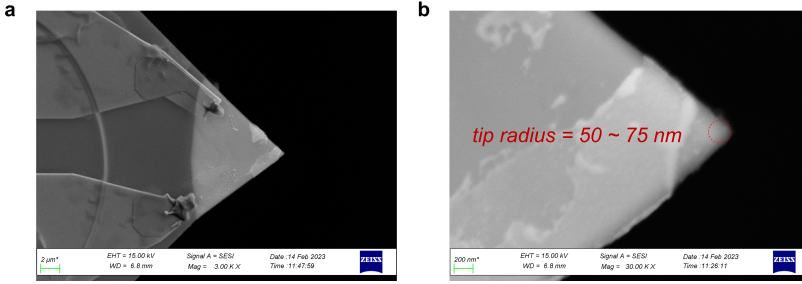


Figure 4.5: (a) SEM image of the SThM probe. (b) A zone image of the tip apex and the measured tip radius of 50 nm to 70 nm.

To access the thermal *conductivity* of $\text{Ti}_3\text{C}_2\text{T}_x$, we follow an approach developed in [49, 102, 155]. To this end, a thermal transport model is used to fit the thickness-dependence of the thermal resistance. To extract the relationship between thermal resistance and the thickness of $\text{Ti}_3\text{C}_2\text{T}_x$ flakes, we performed a pixel-to-pixel correlation of height and thermal maps to create 2D histograms (see Figure 4.3e). This method considers all data points – and does not rely on arbitrarily chosen line-cuts – and we process the data statistically, which reduces experimental errors caused by contaminations or artifacts. For the isolated single-layer case, this histogram shows a two-dimensional Gaussian distribution, and we individually fitted the thickness and thermal resistance with Gaussian functions to obtain their mean values and corresponding standard deviations. For example, the monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ has a thermal resistance of $7.2 \pm 0.23 \text{ MK W}^{-1}$. We applied this method to other SThM data of MXene flakes with different thicknesses to create a 2D histogram of

all data as shown in Figure 4.6a. With increasing flake thickness, the thermal resistance increases and approaches the thermal resistance of the bulk $\text{Ti}_3\text{C}_2\text{T}_x$ in the limit of infinite thickness.

We assume a heat transfer mechanism in the tip-MXene substrate channel, which is depicted in Figure 4.6b. The total thermal resistance measured R_{th} is composed of a series of three resistances $R_{\text{th}} = R_{\text{tip}} + R_{\text{int}} + R_{\text{spr}}$, where R_{tip} is the thermal resistance of the tip, $R_{\text{int}} = r_{\text{int}}/(\pi a^2)$ (a is tip radius and r_{int} is the thermal interface resistivity between MXene and SiO_2) is the tip-sample interface resistance, and R_{spr} is the thermal spreading resistance. We further assume diffusive heat transport for orthotropic thermal spreading in layered $\text{Ti}_3\text{C}_2\text{T}_x$ flakes, according to previous thermal transport studies on other 2D materials [82, 156]. Because the phonon MFPs of MXene (≈ 2 nm) [157] and SiO_2 (≈ 10 nm) [158] are lower than the characteristic length of the SThM probe (tip radius of 75 nm), the probe has a Knudsen number $K(n) \ll 1$, which is well described by the diffusive heat transport. The orthotropic system has thermal conductivities dependent on the direction in the plane (κ_i) and the direction between planes (κ_c). MXenes are anisotropic materials with directional-dependent thermal conductivities. To transform such an orthotropic system to an effective isotropic thermal conductivity, we consider an effective thermal conductivity defined as $\kappa_{\text{eff}} = \sqrt{\kappa_i \times \kappa_c}$ and an effective thickness defined as $t_{\text{eff}} = t \sqrt{\frac{\kappa_i}{\kappa_c}} + r_{\text{int}} \kappa_{\text{eff}}$ (t is the physical thickness). Here, the first term accounts for the anisotropy and the second includes the MXene- SiO_2 interface thermal resistance. Muzychka [101] and Spiece [102] derived an analytical expression for the thermal spreading resistance, as shown in Equation 2.10. For the unknown r_{int} between MXene and SiO_2 , we assume a constant value. A thickness-independent r_{int} has previously been reported in graphene [159] and the same approach has been successfully used to extract the thermal conductivities of graphene [103].

In the end, we quantify the thermal conductivity of $\text{Ti}_3\text{C}_2\text{T}_x$

using the data in Figure 4.6a. The resulting fit is shown in a blue dashed curve, and the fitting parameters are summarized in Table 4.1. For very thin flakes (less than 10 nm), because the radius of the tip (75 nm) is much larger than flake thickness, the heat dissipation channel from the tip to the substrate is almost vertical (cross-plane direction). With this assumption, we can first use an isotropic thermal model (let $\kappa_i = \kappa_c$) to estimate the cross-plane thermal conductivity κ_c . We used this unknown κ_c to fit Equation 2.10 with experimental data (thickness-dependent thermal resistance). In detail, we combined seven 2D histogram maps into one and divided it into multiple small bins. For each column, we selected the bin containing the most data points. The average value of the data in each bin was then used for fitting. When it reached the best fit, we extracted the value of κ_c . Then we used this κ_c value to fit thicker flakes, we considered the orthotropic model to calculate the total thermal resistance $R_{th} = R_{tip} + R_{int} + R_{spr}$ and used the unknown parameters κ_i , r_{int} and R_{tip} to fit the experimental data R_{th} . As a result, we obtained the κ_i , κ_c , r_{int} and R_{tip} values. In detail, we find an interfacial thermal resistance between $Ti_3C_2T_x$ and SiO_2 of r_{int} of $1.0 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$, which is lower than the reported values of interface MoS_2/SiO_2 [160], and close to that of interface $graphene/SiO_2$ [161]. Such a low r_{int} greatly improves the sensitivity and reliability of our SThM measurements [162]. Furthermore, we obtain $\kappa_i = 0.85$ to $1.56 \text{ W m}^{-1} \text{ K}^{-1}$ and $\kappa_c = 0.38$ to $0.63 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. Thus, the effective thermal conductivity $\kappa_{eff} = 0.78 \pm 0.21 \text{ W m}^{-1} \text{ K}^{-1}$ is lower than the $\kappa = 1.4 \text{ W m}^{-1} \text{ K}^{-1}$ of SiO_2 , which is consistent with the contrast observed on the SThM maps (see Figure 4.3c).

We further compared our results with theoretical calculations. For example, Gounzari et al. calculated the thermal conductivity at room temperature to be less than $12 \text{ W m}^{-1} \text{ K}^{-1}$ based on Boltzmann transport theory [163]. Similarly, Gholivand et al. investigated the effect of surface terminations on the thermal conductivity of $Ti_3C_2T_x$ using density functional theory and the phonon Boltzmann transport

Table 4.1: Extracted fitting parameters through a diffusive thermal transport model

Material	κ_i [$\text{W m}^{-1} \text{K}^{-1}$]	κ_e [$\text{W m}^{-1} \text{K}^{-1}$]	κ_{eff} [$\text{W m}^{-1} \text{K}^{-1}$]	r_{int} [$\text{K m}^2 \text{W}^{-1}$]	R_{tip} [K W^{-1}]
$\text{Ti}_3\text{C}_2\text{T}_x/\text{SiO}_2$	0.85 to 1.56	0.38 to 0.63	0.78 ± 0.21	1.0×10^{-8}	3.54×10^6

equation. The O-terminated MXene has lowest thermal conductivity of $11 \text{ W m}^{-1} \text{K}^{-1}$ while F-terminated MXene has highest value of $108 \text{ W m}^{-1} \text{K}^{-1}$ [39]. The measured thermal conductivity of $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes is lower than the values predicted by simulations, which is common in many 2D materials [40]. This is because the additional phonon scattering mechanisms during the measurements, such as defects, interface or boundary scattering are typically not considered in the theoretical calculations.

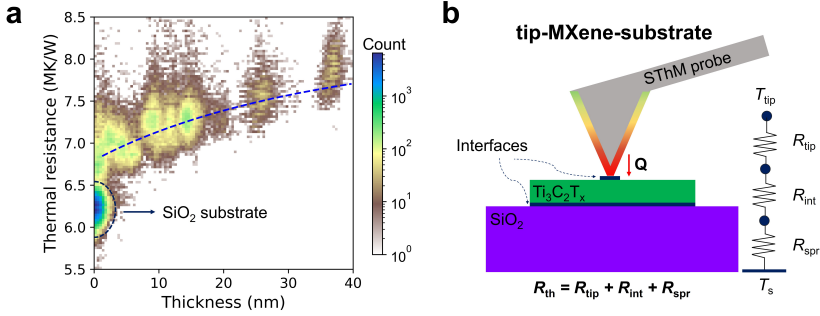


Figure 4.6: (a) Total 2D histogram combined with all different $\text{Ti}_3\text{C}_2\text{T}_x$ thicknesses and the final fit curve (blue line) through a diffusive thermal transport model to extract thermal properties of $\text{Ti}_3\text{C}_2\text{T}_x$. (b) Schematic of the nanoscopic tip-sample contact and the heat transport model in the tip-MXene-substrate channel used in our experiments.

4.5 Evaluation of the electrical conductivity of $\text{Ti}_3\text{C}_2\text{T}_x$

Surprisingly, the thermal conductivity of $\text{Ti}_3\text{C}_2\text{T}_x$ is almost one order of magnitude smaller than the value estimated using the WF law, where contributions from phonons are neglected: by using the electrical resistance $3.18 \text{ k}\Omega$ measured in Figure 4.7, we can estimate the electrical conductivity of $\text{Ti}_3\text{C}_2\text{T}_x$ according the geometry of the flake. We evaluated the average flake length (l) and width (w) of the $\text{Ti}_3\text{C}_2\text{T}_x$ device in Figure 4.1c via optical microscopy with values of $11.64 \text{ }\mu\text{m}$ and $4.59 \text{ }\mu\text{m}$. The AFM-measured thickness of the flake is 1.8 nm , which is higher than the theoretical value of 0.98 nm . That is attributed to the surface absorption of water molecules, solvated ions, etc., between MXene and the substrate [32]. We used the entire thickness in electrical conductivity measurement, similar to what we did in thermal conductivity measurements. The resistance of the flake was obtained from I-V curve (Figure 4.7). It is possible to calculate the sheet resistivity and electrical conductivity of the device by the following formula:

$$\rho = R \cdot \frac{w \cdot t}{l}. \quad (4.2)$$

we obtain an electrical conductivity of $\sigma = 4.43 \times 10^5 \text{ S m}^{-1}$ at room temperature [164], which is comparable to literature values reported for $\text{Ti}_3\text{C}_2\text{T}_x$ single flakes[165]. Although two-terminal contacts were used for the electrical conductivity measurements, which contain contributions from the contact resistance, the impact on our findings is minor: 1) due to their metallic character, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene should form good contacts with indium/gold; 2) ignoring the contact resistance will UNDERestimate σ , and thus the violation of the WF law. Here, we used the entire thickness of the flake (measured by AFM) instead of the theoretical value (0.98 nm) in electrical measurement. And still, we observe the breakdown of the WF law. Using Equation 4.1 we can estimate $\kappa_{\text{WF}} = 3.17 \text{ W m}^{-1}$

K^{-1} , and thus an effective Lorenz number of $L = 0.25L_0$. We note that the average values were used for both electrical and thermal conductivities to estimate the WF law. Since we measured the thermal conductivity of monolayer MXene, we can think this value is in-plane conductivity. So we further estimated the in-plane WF law using these in-plane values, and obtained an effective Lorenz number of $L = 0.3\text{--}0.5L_0$. This strong violation of the WF law will be discussed in the following section.

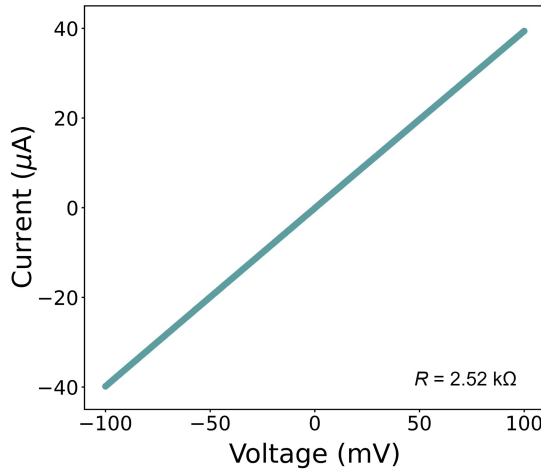


Figure 4.7: I-V curve obtained from two-terminal $\text{Ti}_3\text{C}_2\text{T}_x$ device at the zero gate voltage.

4.6 Violation of the WF law

The thermal conductivity of a material contains contributions from electrons (κ_e) and phonons (κ_{ph}): $\kappa_{\text{eff}} = \kappa_e + \kappa_{\text{ph}}$. Since $\text{Ti}_3\text{C}_2\text{T}_x$ displays a metallic nature with a high density of electronic states near the Fermi level, we can assume that the total thermal conductivity is dominated by electron contributions ($\kappa_e = \kappa_{\text{eff}} = 0.78 \text{ W m}^{-1} \text{ K}^{-1}$), and therefore the WF law should be valid. However, even under this

assumption – by neglecting the phonon contribution – the resulting electronic thermal conductivity is still too low to satisfy the WF relation, indicating a clear violation of the WF law. The WF law is a consequence of Fermi liquid theory and has been verified in numerous metals, such as gold or copper, where transport can be successfully described by weakly interacting Landau quasiparticles. In recent years, several violations of the WF law have been reported in strongly correlated systems with strong inelastic scattering of quasiparticles, where the Fermi liquid theory breaks down. Such systems involve graphene at the charge neutrality point [56], or some transition metal compounds [151].

Usually, IV- and V-group MXenes (especially $\text{Ti}_3\text{C}_2\text{T}_x$) are metallic with high free carrier densities ($\approx 10^{22} \text{ cm}^{-3}$), which drastically enhances interactions between charge carriers and phonons. This was confirmed in recent experimental studies [35, 36, 152] that have provided evidence of strong correlations in MXenes. Using ultra-fast spectroscopy techniques, an electron-phonon coupling strength two orders of magnitude greater than that typically found for conventional metal counterparts was measured in $\text{Ti}_3\text{C}_2\text{T}_x$. Such strong electron-phonon coupling was further observed theoretically and experimentally in another MXene, Nb_2C [166]. Furthermore, high photothermal conversion efficiencies [167] and high phonon frequencies [36] were found in $\text{Ti}_3\text{C}_2\text{T}_x$, which also indicate strong electron-phonon coupling.

These strong correlations found in $\text{Ti}_3\text{C}_2\text{T}_x$ might reveal the mechanism responsible for the violation of the WF law observed in our experiments. Electron-phonon coupling is mainly induced by transverse optical (TO) and longitudinal optical (LO) phonon modes via the short-range deformation potential and the long-range Fröhlich interaction, respectively. Previous studies [25, 36] indicate strong electron-TO coupling but weak electron-LO coupling in $\text{Ti}_3\text{C}_2\text{T}_x$ with a higher density of states of TO modes. Energetic electrons strongly interact with TO phonons, which introduces an additional energy dissipation pathway. The weak electron-LO coupling

suggested the formation of large polarons based on the Fröhlich polaron theory, which increases the effective mass and decreases charge mobility. These behaviors could be attributed to the reduction of κ_e and the breakdown of the WF law. In addition, κ_e and κ_{ph} may potentially be coupled because of the strong electron-phonon interaction. A theoretical calculation [39] predicted the κ_{ph} of $Ti_3C_2T_x$ ranging from $11 \text{ W m}^{-1} \text{ K}^{-1}$ (with the oxygen surface group) to $108 \text{ W m}^{-1} \text{ K}^{-1}$ (with the fluorine surface group). In our experiment, we expected a mixture of three kinds of surface terminations (-F, -OH, =O). The measured thermal conductivity is still much lower than the calculated values, which consider phonon-phonon and boundary scatterings. This suggested that local defects and inelastic electron-phonon scattering processes may result in a large limitation of the phonon heat transport and a further reduction of κ_{ph} . Therefore, we conclude that the ultralow thermal conductivity of $Ti_3C_2T_x$ single flakes is mainly caused by strong electron-phonon interactions. To strengthen our claim, future experiments should be performed to show the difference between the electronic mean free paths (MFPs) for charge transport (l_e) and for thermal transport (l_{th}). For l_e , according to Drude model, we have $l_e = v_F \frac{m^* \sigma}{ne^2}$. For l_{th} , we could calculate it from this relation: $\kappa_e = \frac{1}{3} C_e v_F l_{th}$.

4.7 Thermal management applications

$Ti_3C_2T_x$ shows an ultralow thermal conductivity of $0.78 \text{ W m}^{-1} \text{ K}^{-1}$ and an infrared emissivity of 0.06 [168], which makes it a good candidate for thermal management applications, such as thermal barrier coatings. We estimated its thermal performance (measured in terms of heat loss) and compared it with some typical metals. Considering heat loss mainly involves through two ways: heat conduction and radiation. Based on the Fourier's law and Stefan-Boltzmann law,

Table 4.2: Material’s properties used in heat loss calculations [168–170].

Materials	Heat conduction		Radiation		Q [MW]
	κ [$\text{W m}^{-1} \text{K}^{-1}$]	$T_h - T_c$ [K]	ε	$T_h^4 - T_c^4$ [K^4]	
MXene	0.78	100	0.06	1.67×10^{10}	0.08
Antimonial Lead	30	100	0.43	1.67×10^{10}	3.0
Cold Rolled Steel	45	100	0.75	1.67×10^{10}	4.5
Cast Iron	52	100	0.95	1.67×10^{10}	5.2
Unoxidized Nickel	106	100	0.19	1.67×10^{10}	10.6
Oxidized Brass	111	100	0.61	1.67×10^{10}	11.1
Galvanized Zinc	123	100	0.28	1.67×10^{10}	12.3
Oxidized Aluminum	237	100	0.31	1.67×10^{10}	23.7
Gold	327	100	0.02	1.67×10^{10}	32.7
Rolled Copper	412	100	0.64	1.67×10^{10}	41.3

the total heat loss Q is calculated by the below equation:

$$Q = \frac{\kappa A(T_h - T_c)}{t} + \varepsilon \sigma A(T_h^4 - T_c^4). \tag{4.3}$$

Where κ is thermal conductivity, A is material’s surface area, T_h and T_c is the hot and cold side absolute temperature, t is thickness, ε is emissivity coefficient, σ is Stefan-Boltzmann constant.

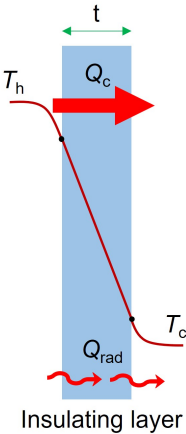


Figure 4.8: Heat transfer model for heat loss calculations.

We assume a heat loss model (Figure 4.8) that in a unit area, heat dissipates to an ambient environment ($T_c = 295$ K) from a higher temperature with a temperature difference of 100 K, and the thickness of materials layer is 1 mm. The detailed properties of these materials are listed in Table 4.2. $\text{Ti}_3\text{C}_2\text{T}_x$ MXene has much lower thermal conductivity and emissivity coefficient than metals, it will contribute to a lower heat loss according to Equation 4.3. Low infrared emission can suppress radiative heat loss. When the thickness is small, heat conduction dominates the heat loss. (Far-field) Radiative heat loss is enhanced at high temperatures due to its T^4 relationship. Therefore, MXene will be a promising thermal insulator over a wide temperature range.

We further compared the resulting in-/cross-plane thermal conductivities of $\text{Ti}_3\text{C}_2\text{T}_x$ with other single-crystalline 2D materials with similar thickness, including isolated mono- or few-layer flakes and thin films (Figure 4.9a). Compared to other 2D materials, $\text{Ti}_3\text{C}_2\text{T}_x$ shows a record low thermal conductivity, especially in in-plane direction. The low thermal conductivity found in $\text{Ti}_3\text{C}_2\text{T}_x$ makes the material attractive for thermal insulation or infrared stealth applications, and we compared its thermal insulation performance (heat loss) with other common metals in thermal management applications (Figure 4.9b). The heat loss of $\text{Ti}_3\text{C}_2\text{T}_x$ is two orders of magnitude smaller than common metals, such as gold, aluminium and steel, which shows great potential for use as a good thermal barrier in electronic devices and a large variety of other applications. Replacing polished metal casing of industrial equipment with $\text{Ti}_3\text{C}_2\text{T}_x$ foil or use of a submicrometer MXene coating on equipment may save billions of dollars in heat losses.

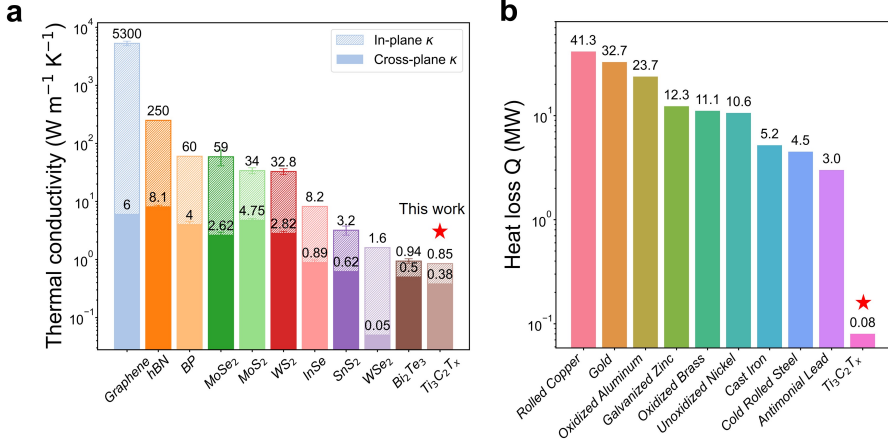


Figure 4.9: (a) Comparison of experimental results in thermal conductivity for several 2D materials with monolayers and few layers, including graphene [171, 172], hBN [173, 174], BP [175], MoSe₂ [176, 177], MoS₂ [177, 178], WS₂ [177, 179], InSe [49, 86], SnS₂ [180, 181], WSe₂ [149, 182], Bi₂Te₃ [183, 184], and our work on Ti₃C₂T_x. (b) Comparison of the heat loss for Ti₃C₂T_x MXene and other common metals in thermal management applications

4.8 Conclusion

We experimentally quantified the anisotropic thermal transport properties of isolated single-crystalline Ti₃C₂T_x flakes by combining scanning thermal microscopy at room temperature and a diffusion heat transfer model. An ultralow thermal conductivity of $\kappa_{\text{eff}} = 0.78 \pm 0.21 \text{ W m}^{-1} \text{ K}^{-1}$ was observed. Given the high electrical conductivity of $\sigma = 4.43 \times 10^5 \text{ S m}^{-1}$ found in our samples, we reveal a strong violation of the WF law, with an effective Lorenz number $L = 0.25L_0$. We attribute this violation to the strong electron-phonon coupling in Ti₃C₂T_x, especially the electron-LO scattering which suppresses the electronic thermal conductivity. In addition,

local defects or phonon scatterings can reduce the phononic thermal conductivity. To this end, we observed an ultra-low total thermal conductivity. These results provide an experimental basis showing that MXenes are very promising materials for future thermoelectric applications thanks to a high electrical conductivity combined with high thermal resistivity. Furthermore, this work highlights the application potential of $Ti_3C_2T_x$ for thermal management or – thanks to its very low infrared emissivity [168] – for thermal barrier coatings.

4.9 Thermal transport measurements on other MXene flakes

4.9.1 Thermal transport in Mo_2CT_x

We also performed SThM measurements on Mo_2CT_x and V_2CT_x MXenes. As discussed in the MXene synthesis section, Mo_2CT_x was synthesized from a Ga-based MAX phase, which required more aggressive reaction conditions, such as high temperature and pressure and long etching time. This causes the high surface roughness and numerous defects in the Mo_2CT_x flakes, which results in measurement errors and artifacts during SThM thermal transport measurements. Figure 4.10 shows the AFM and SThM maps of Mo_2CT_x flakes. As we can see, the SThM map exhibits strong signal fluctuations, which makes quantitative thermal analysis very difficult and introduces large uncertainty into the results. So we do not use a thermal transport model to quantitatively investigate the thermal properties of Mo_2CT_x flakes. Because a smooth and clean surface is crucial for accurate thermal measurements of two-dimensional layered materials, further synthesis of higher-quality Mo_2CT_x MXene flakes is necessary to enhance the precision of thermal measurements.

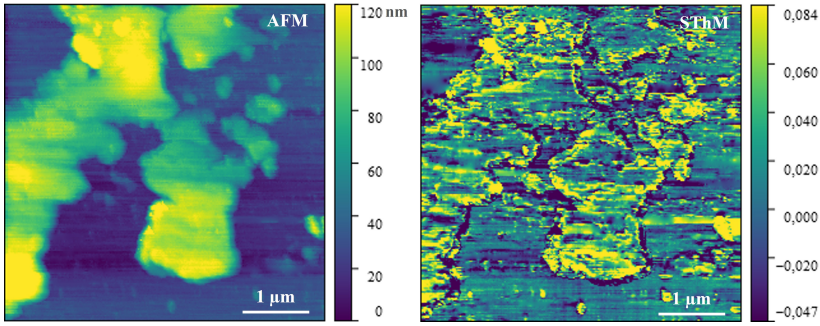


Figure 4.10: (a) AFM and (b) SThM maps of Mo_2CT_x flakes.

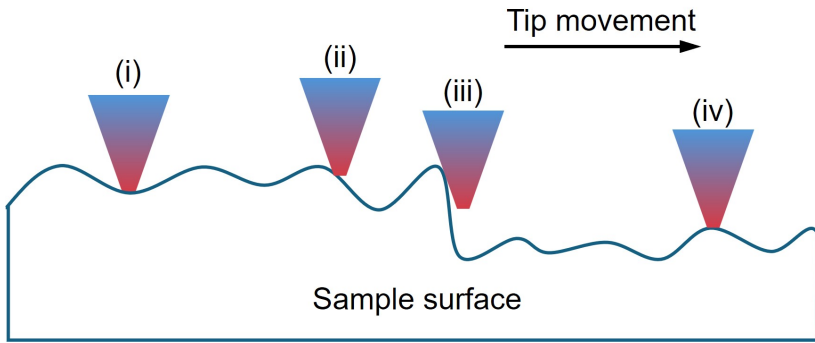


Figure 4.11: Possible SThM probe contacted with sample according to the surface roughness.

The surface roughness of the measured sample is an important parameter to affect the SThM thermal measurements. As shown in Figure 4.11, the contact area between the probe tip and the sample surface may vary during scanning due to surface roughness. In cases (i) and (iv) of the figure, where the surface is relatively uniform and the tip radius is larger than the height variation (gap), the contact between the tip and the sample surface (described in chapter 2) is a good solid–solid contact, possibly with a water meniscus present at the interface. However, when the surface contains a very high

step, the tip loses contact with the surface, and the contact area may shift to the side of the probe, as shown in case (iii). The heat transfer in this case would be fully changed. In addition, in case (ii), the contact area between the tip and the sample changes (typically, with a reduced contact radius), which results in a reduced heat transfer from the tip to the sample. Because the thermal transport model is challenging to derive for cases (ii) and (iii), it is preferable to avoid these cases during SThM measurements and further adopt a statistical method to analyze the data, as previously discussed for $Ti_3C_2T_x$ MXene.

4.9.2 Thermal transport in V_2CT_x

As one of the V-based MXenes, the electrical and optical properties of V_2CT_x have been reported, but its thermal properties also require investigation to enable the development of various functional devices. Due to the small size of the V_2CT_x flakes, SThM technique is the optimum choice to understand nanoscale thermal transport in the V_2CT_x flakes. We apply the same SThM measurements previously used on $Ti_3C_2T_x$ MXene. To study the thickness-dependent thermal resistance of the V_2CT_x flakes, we selected a large scan area containing flakes of varying thicknesses. As shown in Figure 4.12, the thermal resistance increases with the increasing thickness of the MXene flakes.

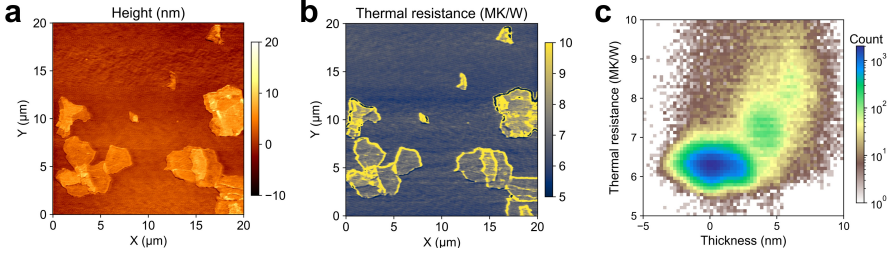


Figure 4.12: (a) Topography and (b) thermal resistance maps of a few layers V_2CT_x on SiO_2 acquired under ambient environment. (c) 2D histogram profile showing the relationship between thickness and thermal resistance of the entire image.

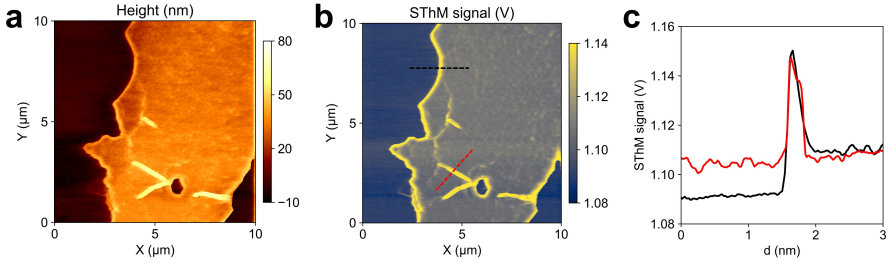


Figure 4.13: (a) Topography and (b) SThM maps of a V_2CT_x flake with defects (wrinkles and holes). (c) Linecut curves indicated in (b).

In addition, when transferring V_2CT_x MXene flake on SiO_2 substrate, wrinkles or holes often form due to the mechanical flexibility and fragility of the flakes. We also investigate the impact of these wrinkles or holes on thermal transport properties in MXene flakes. Figure 4.13a shows the topography image of a V_2CT_x flake on SiO_2 substrate with a few wrinkle and holes. Higher SThM signals are observed around the edges, wrinkles, and holes (Figure 4.13b and 4.13c), indicating a increase in the tip-sample thermal resistance.

This can be attributed to a decrease in the phonon mean free path (MFP) and a reduced tip-sample contact radius when the tip scans over the edges, wrinkles, and holes, leading to increased thermal resistance in these regions.

4.9.3 Summary

In this section, the thermal properties of two additional MXenes (Mo_2CT_x and V_2CT_x) were studied using the SThM method. The SThM signal was found to vary with changes in the thickness of the MXene flakes as well as the presence of local defects such as wrinkles and holes. In real measurement, the solid-solid contact between the tip and the sample is never ideal due to the surface roughness of the sample. Artifacts arising from this surface roughness were also observed and are discussed. A bad thermal contact between tip and sample will limit the sensitivity of SThM and prohibit the accurate extraction of local thermal conductance values. Therefore, the extraction of the thermal conductivity of MXenes using SThM presents several critical challenges, including the need for accurate thermal exchange modeling and precise calibration protocols. High-quality MXene flakes and well-defined thickness changes help simplify the heat transfer model and enable more reliable quantitative analysis.

Chapter 5

Thermoelectric properties of single $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes

When monolayers of MXenes are stacked into van der Waals junctions, such as MXene films or heterostructures, interlayer interaction can significantly influence the transport properties and even introduce new properties. Probing the local thermoelectric transport of MXene homostructures offers a direct approach to uncover the underlying interlayer interaction mechanism. However, experimental investigations remain limited owing to challenges in measuring the thermoelectric transport properties in MXene single flakes. In this chapter, we will study the local Seebeck effect in $\text{Ti}_3\text{C}_2\text{T}_x$ homostructures at room temperature using on-chip thermoelectric devices and SThM technique.

5.1 Introduction

Two-dimensional (2D) transition metal carbides and nitrides (MXenes) have emerged as promising candidates for a wide range of ap-

plications—including electromagnetic interference shielding, flexible electronics, energy storage, thermal management, and sensing—due to their highly tunable electronic properties and exceptional chemical stability [4, 7, 54]. For large-scale applications, MXenes are typically processed into macroscopic layered assemblies, such as freestanding films composed of stacked single-crystalline flakes [185–188]. The performance of these assemblies is governed not only by the intrinsic properties of individual flakes but also critically by the nature of interlayer interactions, which impact key transport phenomena—electrical, thermal, and thermoelectric alike [189, 190].

In homostructured MXene films, adjacent flakes are held together predominantly by van der Waals (vdW) forces and hydrogen bonding through surface terminations (*e.g.*, $-\text{OH}$, $-\text{F}$, $=\text{O}$) introduced during wet chemical synthesis [191]. While the in-plane charge transport in $\text{Ti}_3\text{C}_2\text{T}_x$ and other MXenes has been extensively explored through both experimental and theoretical approaches [164, 192, 193], the fundamental mechanisms governing inter-flake coupling in stacked structures remain poorly understood. In particular, direct experimental insights into how these interlayer interactions influence transport properties are still lacking.

Probing local thermoelectric behavior offers a powerful approach to elucidate such interlayer effects [132, 194, 195]. When a temperature gradient is applied across a multilayer MXene film, charge carriers diffuse from the hot to the cold side (Figure 5.1a). Unlike single-layer MXene, where transport is dominated by intra-flake conduction, multilayer structures introduce additional transport pathways—including interlayer hopping [25] and increased interface scattering due to potential barriers between flakes [157]. In the absence of inter-flake coupling, the total Seebeck coefficient S_{tot} would be expected to match that of a single flake (S_1), as shown in Figure 5.1b. However, strong interlayer interactions can substantially alter the local electronic band structure and carrier scattering timescales near the Fermi level (Figure 5.1c), resulting in $S_{\text{tot}} \neq S_1$.

These interlayer effects can be influenced by a range of factors,

including carrier density (or local density of states), interface-induced scattering, electronic hybridization, and flake thickness. Analogous behavior has been reported in other 2D material systems such as graphene [196] and transition metal dichalcogenides (TMDs) [197], where stacking-induced modifications to thermoelectric and transport properties reveal the critical role of interlayer physics.

However, despite several studies on the macroscopic thermoelectric behavior of MXene films, direct experimental investigations of thermoelectric effects at the level of individual MXene flakes remain scarce [198]. This is primarily due to the experimental challenges associated with precisely manipulating and characterizing the nanoscale flakes—typically smaller than $10\text{ }\mu\text{m}$ —produced via liquid-phase synthesis.

Here, we investigate the thickness-dependent thermoelectric properties of $\text{Ti}_3\text{C}_2\text{T}_x$ by fabricating vertically stacked monolayers with a precisely controlled number of layers, using a modified dry-transfer technique. At room temperature, the Seebeck coefficient (S) of these MXene homostructures exhibits a pronounced increase with layer number, reaching values of $-2.54\text{ }\mu\text{V K}^{-1}$ for bilayers and $-5.50\text{ }\mu\text{V K}^{-1}$ for trilayers—representing enhancements of approximately 100% and 330%, respectively, compared to monolayers. These substantial deviations from monolayer behavior point to a critical role of interlayer interactions in modulating thermoelectric response.

To further probe these effects at the nanoscale, we employ scanning thermal microscopy (SThM) to spatially resolve local thermoelectric properties across MXene homojunctions. Using a deconvolution-based reconstruction method, we generate high-resolution maps of the local Seebeck coefficient, revealing spatial S variations correlated with flake thickness, local defects and surface termination distribution. Our results offer new insights into the interlayer coupling mechanisms in stacked MXene systems and provide a pathway for tailoring thermoelectric properties in 2D materials through vertical assembly and interface engineering.

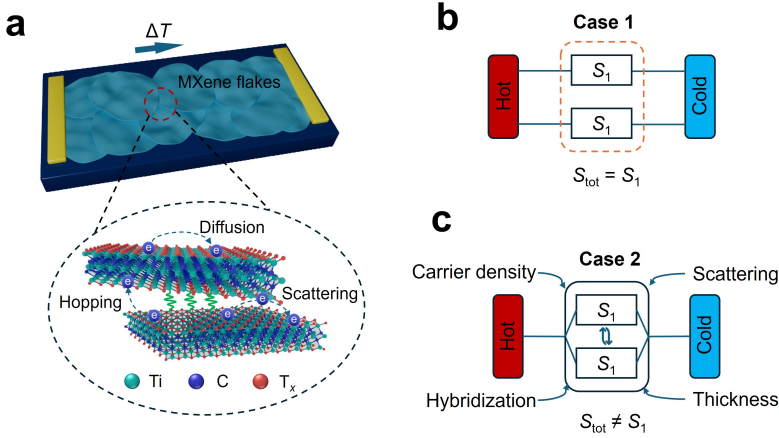


Figure 5.1: (a) Transport properties of MXene flakes under a temperature gradient, electrons behaviors in intra- and inter-flakes. (b) $S_{tot} = S_1$ due to the independent transport of different layers (c) $S_{tot} \neq S_1$ due to the interlayer interactions related to the DOS, interlayer scattering, hybridization effects and thickness of MXene flakes.

5.2 Measurement setups

As mentioned previously, two main measurement setups (on-chip micro-heater bridge and SThM method) are used in this work. On-chip measurement probes the global thermoelectric properties along the MXene device. While SThM method allow us scan over the sample to locally study its thermoelectric properties. These two methods are schematically shown in Figure 5.2. Both AC (2ω) and DC measurements can be used for the two methods. For AC measurements in this chapter, the heater is driven at a low frequency of ω and generated a temperature gradient along the sample at a frequency of 2ω . The thermovoltage induced by this temperature gradient is then measured at the second harmonic using a lock-in

amplifier. For DC measurements, a direct DC power is applied to the heater and causes a constant temperature gradient. The thermovoltage is recorded via a pre-amplifier. The detail device fabrication and measurement methods are described in the following.

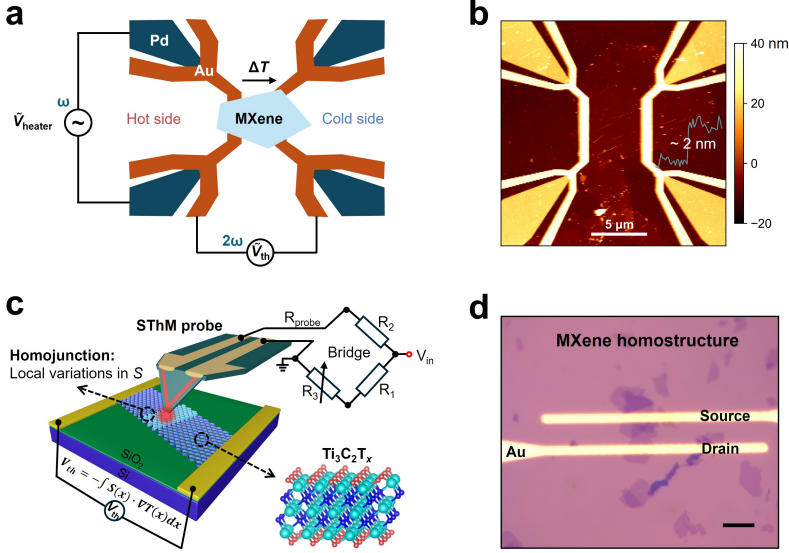


Figure 5.2: (a) Schematic of thermoelectric measurement of $\text{Ti}_3\text{C}_2\text{T}_x$ single flake on the pre-patterned device. (b) AFM image of the stamping $\text{Ti}_3\text{C}_2\text{T}_x$ single flake on the pre-patterned device. Scale bar: $10\ \mu\text{m}$. (c) Schematic of local thermoelectric measurement on the $\text{Ti}_3\text{C}_2\text{T}_x$ homostructure using SThM setup. (d) Optical image of the $\text{Ti}_3\text{C}_2\text{T}_x$ homostructure device on gold contacts. Scale bar: $10\ \mu\text{m}$.

5.2.1 $\text{Ti}_3\text{C}_2\text{T}_x$ MXene preparation and device fabrication

$\text{Ti}_3\text{C}_2\text{T}_x$ MXene colloid ($\sim 40\ \text{mg/mL}$) was provided by our collaborator. It was then diluted with deionized (DI) water to obtain

monolayer and few-layer $\text{Ti}_3\text{C}_2\text{T}_x$ aqueous solution for use. The $\text{Ti}_3\text{C}_2\text{T}_x$ homostructure junction was formed by drop-coating the solution onto a SiO_2/Si wafer (290 nm top-layer SiO_2). The wafer was washed with DI water and blown dry with nitrogen and then completely dried in an oven at 60°C . We can find $\text{Ti}_3\text{C}_2\text{T}_x$ homostructure junctions with several single flakes stacking together randomly under the optical microscopy (Figure 5.10). Indium needles [147] were fabricated in $\text{Ti}_3\text{C}_2\text{T}_x$ homojunctions as electrodes for thermovoltage measurements. Additionally, another MXene homostructure device for SThM AC measurement was fabricated through a controlled flake stacking process on pre-patterned gold contacts, as shown in Figure 5.2d and detailed below.

On-chip thermoelectric device was fabricated by the following steps: pre-patterned heaters and contacts are achieved by standard electron beam lithography and electron beam evaporation. The heaters (3 nm Ti/27 nm Pd) were first patterned on SiO_2/Si wafer and then covered by 10 nm Al_2O_3 insulating layer via atomic layer deposition. Four-terminal contacts (3 nm Ti/47 nm Au) were finally deposited as top electrodes and thermometers. $\text{Ti}_3\text{C}_2\text{T}_x$ single flake was transferred to the pre-patterned device via polymer-based dry stamping method (see chapter 3 in detail). The same process for stamping another MXene single layer on top to achieve layer-by-layer assembly MXene devices with different thicknesses. The final thermoelectric device layout is shown in Figure 5.3.

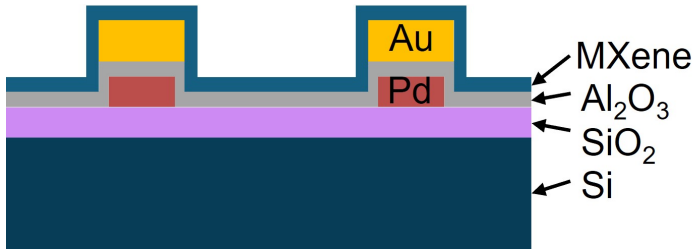


Figure 5.3: Schematic of the final MXene thermoelectric device (side view).

5.2.2 Thermoelectric measurements on micro-bridge devices

We first study the S of $\text{Ti}_3\text{C}_2\text{T}_x$ single flake with an on-chip thermoelectric device architecture (Figure 5.2a). This micro-structured device contains pre-patterned top gold contacts (also acting as thermometers), bottom palladium microheaters and an intermediate Al_2O_3 thin film for electrical insulation. $\text{Ti}_3\text{C}_2\text{T}_x$ monolayer was stamped using a dry transfer method [146]. The device structure and topography was confirmed by optical (Figure 5.6a) and AFM image (Figure 5.2b), showing a flake thickness of 2 nm. This thickness matches the thickness of the reported $\text{Ti}_3\text{C}_2\text{T}_x$ monolayer with 1.5 nm to 2 nm in AFM measurements [199]. To measure S of the $\text{Ti}_3\text{C}_2\text{T}_x$ flake, we applied an AC voltage $\tilde{V}_{\text{heater}}$ at frequency ω to the microheater which induces a temperature difference between the hot and the cold side $\Delta T = T_{\text{hot}} - T_{\text{cold}}$. A low-frequency ($f = 3 \sim 17$ Hz) voltage was used to ensure that the system was slow enough to achieve thermal equilibrium [200]. The thermovoltage ($\tilde{V}_{\text{th}}$) at frequency of 2ω (second harmonic) was then demodulated using a lock-in technique and the Seebeck coefficient of $\text{Ti}_3\text{C}_2\text{T}_x$ flake could be extracted by the equation: $S = -\tilde{V}_{\text{th}} / \Delta T$. To this end, an AC voltage $\tilde{V}_{\text{heater}}$ (the power is ranging from 0 to 0.5 mW) at a very low frequency of $\omega = 3$ Hz was applied to the Pd heater. The induced thermovoltage between source and drain contacts was pre-amplified by a SR560 low-noise preamplifier and demodulated at a frequency of $2\omega = 6$ Hz by a MFLI lock-in to obtain $\tilde{V}_{\text{th}}$ at different heater power. It is worth to note that the peak signal in second harmonic (2ω) has a 90° phase shift with respect to the excitation (ω). Besides, the lock-in displays the rms signal and the reference is around half of the $\tilde{V}_{\text{th}}$ but we need to use the peak-to-peak signal for $\tilde{V}_{\text{th}}$. To this end, the raw data (Y component at 2ω) need to be multiplied by a total factor of $-2\sqrt{2}$ to correct the $\tilde{V}_{\text{th}}$. To estimate the Seebeck coefficient of $\text{Ti}_3\text{C}_2\text{T}_x$ flake, we also need to know the temperature difference ΔT along the flake. The detailed ΔT calibration is shown

in the following Section 5.3.

5.2.3 SThM measurements on $\text{Ti}_3\text{C}_2\text{T}_x$ MXene homostructure

Because the S is highly sensitive to the electronic DOS near to the Fermi level, it can be easily affected by local factors such as defects, strain, stacking order and substrate. To further understand the thermoelectric properties of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, we studied local S variations ($S(x)$) in MXene homostructure device via SThM technique (Figure 5.2c). Briefly, we fabricated the MXene homostructure device by transferring single flakes in a SiO_2/Si wafer with pre-patterned gold contacts (Figure 5.2d). Local Joule heating was employed by SThM probe to measure the Seebeck effect across the homojunction. We applied a voltage through home-built Wheatstone bridge to generate a temperature gradient $\nabla T(x)$ along MXene flakes. We then recorded the voltage drop between source and drain contacts and finally mapped the thermovoltage profile when the SThM probe scanned over the device. The measurement detail is presented in chapter 3.

5.3 On-chip thermoelectric characterization

We investigated the thickness effect on thermoelectric properties of MXene flakes by stacking monolayer MXene layer-by-layer (ranging from 1 L to 5 L) on the same thermoelectric platform. Figure 5.6b presents the results of thermoelectric measurements on MXene flakes with different thicknesses, showing a linear thermovoltage response to the applied heater power (P_{heater}). The thermovoltage of the monolayer MXene was first measured and then the devices with different layers were continuously measured via layer-by-layer

stacking. We extracted the slope of 7.64 ± 0.24 , 15.27 ± 0.15 , 33.13 ± 0.12 , 21.94 ± 0.15 , and $20.66 \pm 0.09 \mu\text{V mW}^{-1}$ via a linear regression for 1 L to 5 L devices, respectively. To access S , we estimated ΔT using the resistance thermometer method. We note that this ΔT calibration process is performed after transferring the MXene flake on top. Four-terminal gold contacts was used as the thermometer. ΔT was obtained by calibrating the temperature-dependent resistances of the two gold contacts (hot and cold sides). As illustrated in Figure 5.4, an small AC voltage at 1 kHz was applied across one gold lead in MFLI lock-in, while the current ($\tilde{I}$) was measured from another lead and the internal voltage drop ($\tilde{V}$) was measured simultaneously. The resistance of gold thermometer was calculated as $R = \tilde{V}/\tilde{I}$.

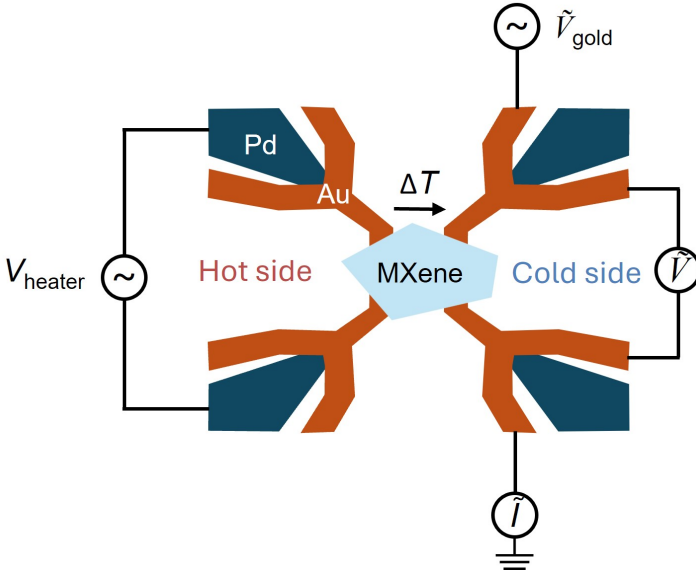


Figure 5.4: Schematic of the calibration of four-terminal gold resistance thermometers.

To extract the ΔT , we need to measure the device resistance

as a function of the temperature and heater power. The four-terminal resistance of gold contacts (both (drain) hot and source (cold) leads) was first measured as a function of bath temperature (T_{bath}) without applying power to the heater (see Figure 5.5a and 5.5b). Temperature Coefficient of Resistance (TCR) of the gold can be described by $TCR = \frac{1}{R_0} \cdot \frac{dR}{dT}$. We linearly fitted the $R - T$ curves of two gold contacts and extracted the slopes, which correspond to the product $TCR \cdot R_0$ of $0.04 \Omega K^{-1}$ for hot and cold contacts. In the following, the bath temperature was held constant, and the four-terminal resistance was measured as a function of heater power (Figure 5.5c and 5.5d). Because Joule heating is directly proportional to P , we linearly fitted the $R - P$ curves and extracted the slopes of $0.26 \Omega mW^{-1}$ and $0.02 \Omega mW^{-1}$ for hot and cold contacts, respectively.

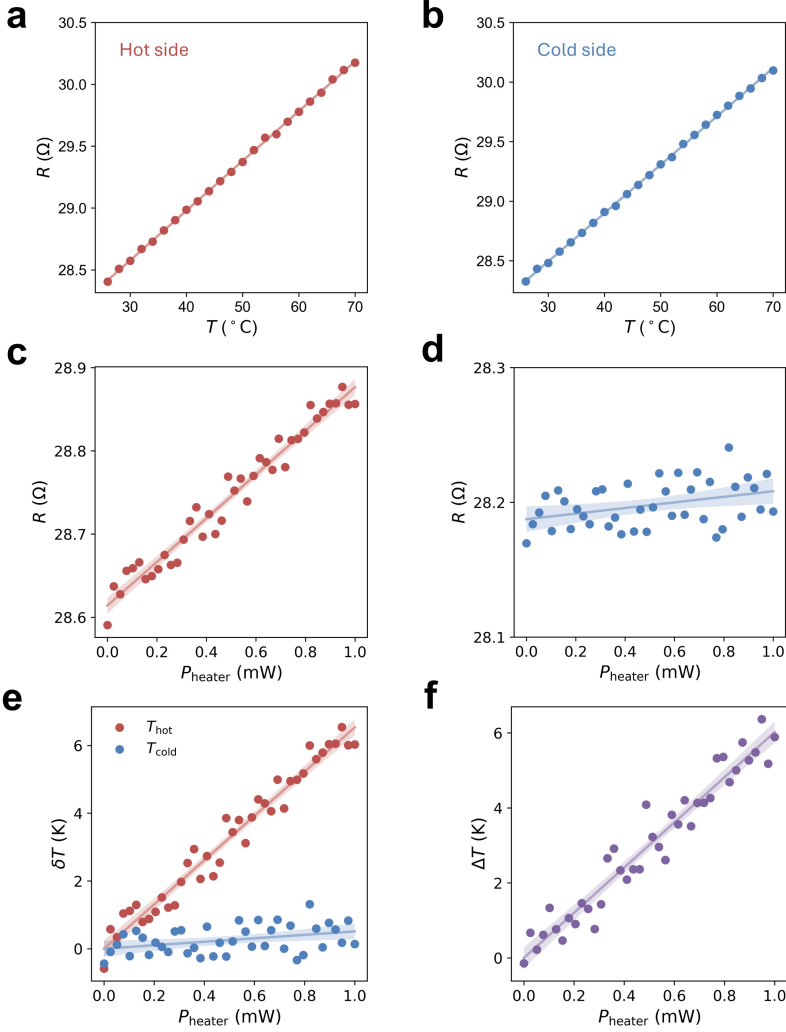


Figure 5.5: Calibration of the gold thermometers. Resistance of the gold contact in the hot side (a) and the cold side (b) as a function of the bath temperature. Resistance of the gold contact in the hot side (c) and the cold side (d) as a function of the applied power to the heater. (e) Extracted temperature jumps δT on the hot and cold leads as a function of P_{heater} . (f) Temperature drop $\Delta T = T_{\text{hot}} - T_{\text{cold}}$ across the MXene flake as a function of P_{heater} .

By combining both measurement results, we could estimate the temperature rise δ_{hot} and δ_{cold} ($T_{\text{cold}} - T_{\text{bath}}$) as a function of P_{heater} (Figure 5.5e). The hot lead that was directly contacted to the microheater heated up a few Kelvins while the cold lead almost stayed at bath temperature. For example, the cold lead only heated up by about 0.5 K at $P_{\text{heater}} = 1$ mW and yields a $\delta T_{\text{cold}} / \Delta T \approx 0.08$, indicating the minimal heating effect of the cold lead and MXene flake. We further estimated ΔT as a function of P_{heater} (Figure 5.5f). It can be seen that ΔT increases linearly with P_{heater} (the extracting slope of 6.02 ± 0.47 K mW $^{-1}$), which allows us to accurately apply a small ΔT by controlling P_{heater} . We finally obtained the Seebeck coefficient $S \approx -1.27, -2.54, -5.50, -3.64$ and -3.43 $\mu\text{V K}^{-1}$ for 1 L to 5 L MXene, respectively (Figure 5.6c). The negative sign of the S indicates the n-type conduction of the MXene. Although $\text{Ti}_3\text{C}_2\text{T}_x$ MXene shows a small room-temperature S value which is comparable to the other common metals because of its metallic feature. The S increases almost by 100% after forming bilayer homostructure and reaches the highest value at 3 L. We observed the same increase in another device (see Figure A.3 in Appendix A). These results may be attributed to the dependence of interlayer interactions with increasing number of layers. In the following, we will further discuss this abnormal layer-dependent S of MXene flakes.

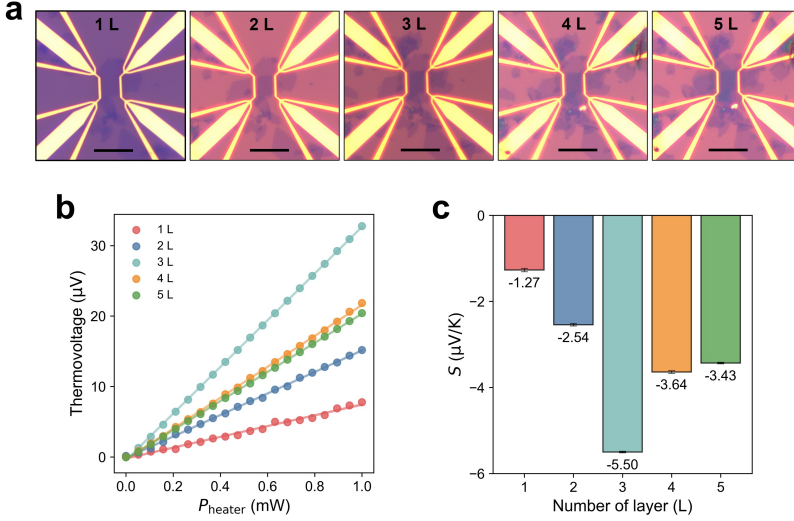


Figure 5.6: (a) Optical images of MXene thermoelectric devices fabricated by sequential transfer of MXene single layers (from 1 L to 5 L). Scale bar: $10\mu\text{m}$. (b) Thermovoltage between hot and cold contacts as a function of heater power P_{heater} . (c) Extracted S of MXene flakes from 1 L to 5 L.

The sign and magnitude of the Seebeck coefficient are highly related to the electronic structure and transport parameters, as defined by the Mott expression. As shown in Equation 2.19 (see chapter 2), there are two mechanisms that can increase S : i) a local increase in DOS; ii) an increase in energy dependence carrier mobility, typically by enhancing the scattering mechanism. The S measures the asymmetry in electronic structure and scattering rates near the Fermi level. Interlayer interaction is commonly found in vdW materials and can induce distinctive properties for multilayer homostructure. As reported in other 2D materials, for example, the band structure of graphene changes near the Fermi level from monolayer to bilayer, leading to different transport properties [201, 202]. Similarly, interlayer hybridization results in bandgaps transition of

TMDs as the number of layers increases [203, 204]. In MXene, the interlayer interaction also plays a crucial role in enhancing the S . One possible interaction is the strong hybridization effects induced by surface terminations [15, 205], which can alter the electronic band structure. This band reconstruction may introduce extra surface states, resulting in the asymmetry in electronic structure and rapidly changing in DOS near the Fermi level. Furthermore, previous studies have shown that the inter-flake charge transport occurs through a small polaron hopping mechanism [25]. This thermally activated hopping can act as an energy filter, filtering out low-energy electrons. We speculate that the interlayer scattering in multilayer further affects the electron scattering time and can thereby contribute to the observed increase in the S . For example, the interlayer misalignment of stacked bilayer induces more phonon vibration modes and increases the carrier's scattering timescale.

Kelvin probe force microscopy (KPFM) image of MXene homostructure is shown in Figure 5.7b. The linecut indicates the surface potential changes from Au substrate to monolayer and stacked bilayer. The work function difference between monolayer and bilayer MXene is around 50 mV for a junction created on Au substrate (Figure 5.7c). This result indicates a shift of the Fermi level when transitioning from monolayer to bilayer and leads to a band bending. Previous experimental evidence further supports the presence of the interlayer interactions of MXene multilayers. Raman spectra of the different thickness MXene flakes showed that the intensity ratios of the out-of-plane (A_{1g}) and in-plane (E_g) modes (A_{1g}/E_g) are gradually decreasing with the increase of number of layers from 1 L to 3 L [83]. This decrease suggests that the enhanced interlayer interactions, caused by the hybridization effect, charge redistribution or interface scattering, restrict the vibration of A_{1g} . Moreover, the elastic modulus of bilayer MXene is approximately twice that of the monolayer, providing further evidence for strong interlayer interactions [32]. Therefore, the observed layer-dependent S mainly reflects variations in the band structure of the MXene.

Such band bending can lead to local changes in the electronic DOS, which in turn results in variations in S .

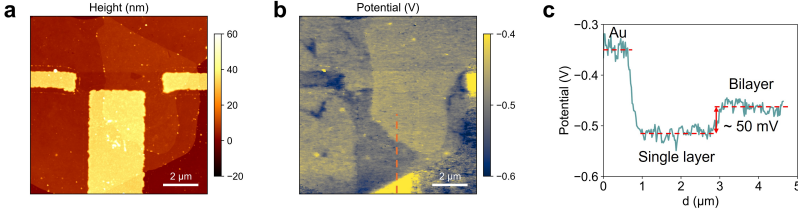


Figure 5.7: KPFM measurements on MXene homostructure. (a) Topography and (b) potential profile of MXene homostructure. The flakes are grounded by gold contacts. (c) KPFM line scan, denoted by a orange dotted line in (b).

5.4 Mapping local thermoelectric effects in MXene homostructure

5.4.1 AC measurements with SThM

To further understand the thermoelectric transport in MXene flakes at nanoscale, we performed local thermoelectric measurements via the SThM technique in the $\text{Ti}_3\text{C}_2\text{T}_x/\text{Ti}_3\text{C}_2\text{T}_x$ homojunction device (Figure 5.2d). This homojunction was formed by two individual MXene flakes self-stacking together, as shown in AFM profiles (Figure 5.8). The formation of the homojunction affects the Seebeck coefficient of the MXene flake and we could observe a thermovoltage response along the junctions. The Seebeck effect is characterized by applying a voltage to the SThM probe. The Joule-heated probe induced a temperature gradient along the MXene flake because of the non-equilibrium heat transport from tip apex to MXene flake. When the heated tip is scanned over the $\text{Ti}_3\text{C}_2\text{T}_x$ device, we record the tip-position dependent open-circuit voltage drop between source and drain contacts, creating a 2D thermovoltage map. For AC

thermovoltage measurements, it is also important to record the phase map in addition to the amplitude. The phase provides information about the sign of the thermovoltage, which cannot be directly obtained from the amplitude alone. This sign depends on both the source/drain electrode configuration (i.e., which contact acts as the source or drain) and the type of majority carriers of MXene. By analyzing the phase, we can determine whether thermovoltage corresponds to a positive or negative Seebeck coefficient.

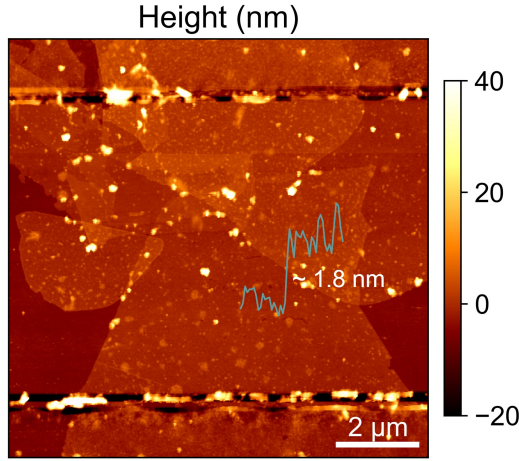


Figure 5.8: AFM image of the MXene homostructure on gold contacts in Figure 5.2d.

We assume no thermoelectric response induced by a temperature gradient along the vertical (y-axis) direction in 2D thermovoltage maps. The measured position-dependent thermovoltage can be described by equation [50]:

$$V_{th}(x_T) = - \int_{x_L}^{x_R} S(x) \frac{\partial T(x - x_T)}{\partial x} dx \quad (5.1)$$

Where x_T is the position of the tip, x_L and x_R are the positions of the left and right contacts, $S(x)$ is the local Seebeck coefficient and

$\frac{\partial T(x-x_T)}{\partial x}$ is the position dependent temperature derivative caused by the hot tip. The measured local V_{th} is given by a convolution of the temperature gradient induced by the hot tip and the spatial Seebeck coefficient distribution along the length of the device, from left to right. We assume a symmetric function of local temperature rise $T(x)$, so V_{th} reflects the asymmetric local $S(x)$ variations in MXene sample around the tip position. We observed a positive phase (Figure 5.9a and 5.9d) and a resulting negative thermovoltage signal (Figure 5.9b and 5.9e) along the junction, where symmetry is broken by the step in the stacking area (Figure 5.9b). This phenomenon can be explained by the difference in Seebeck coefficients between the single layer and stacked bilayer regions of the device $\Delta S = S_{single} - S_{bilayer}$, under an anti-symmetry temperature gradient. $S(x)$ is only dependent on the sample construction and local factors and does not change its spatial distribution as the probe moves. Therefore, $V_{th}(x_T)$ was calculated by integrating $S(x) \frac{\partial T(x-x_T)}{\partial x}$ over the whole device length. As shown in Figure 5.9g, we modeled the thermovoltage map $V_{th}(x_T)$ by assuming a Seebeck difference ΔS between single flake and stacked bilayer and convolute it by Equation 5.1. A line trace from the simulated thermovoltage shows a negative signal, which is in accordance with the measurements (Figure 5.9h). A large thermovoltage was observed when the source and drain contacts were heated up. The sign of the phase depends on both the drain/source configuration and the type of charge carriers in the MXene. Electrons will diffuse from gold contacts into the MXene channel, resulting in a positive (negative) signal at the drain (source) contact. The polarity of the thermovoltage response aligns with electron-dominated thermoelectric transport behavior in MXene. We also observed some bipolar thermovoltage on gold contacts which may result from the inhomogeneity or defects at the interface. In addition, same thermovoltage responses were observed in another device (Figure 5.10) via DC SThM measurement. In the structure of monolayer-bilayer-monolayer junction, we can see a bipolar thermovoltage because of the broken symmetry on both sides.

The detailed characterization will be discussed in the following.

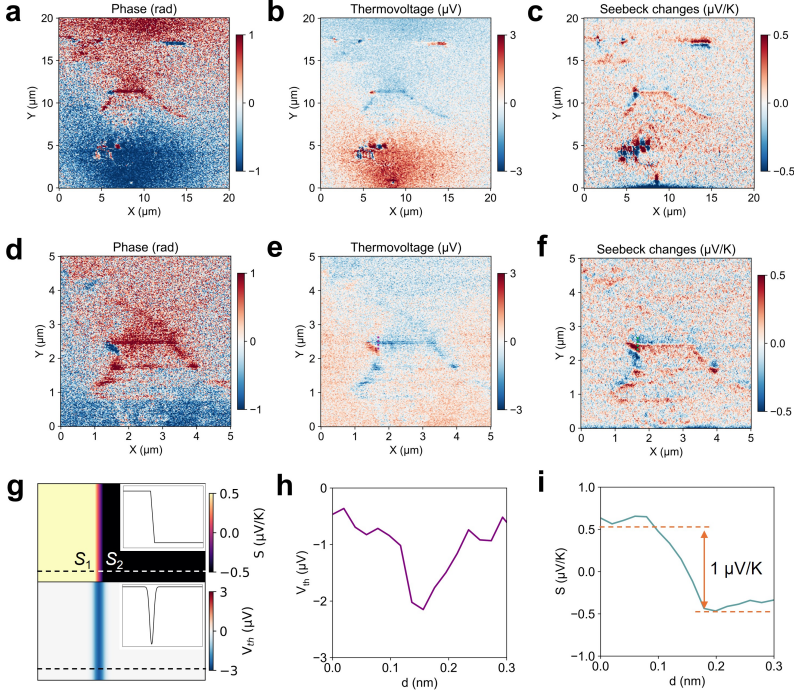


Figure 5.9: (a, d) Phase and (b, e) amplitude of thermovoltage maps and (c, f) extracted Seebeck variation maps of the $Ti_3C_2T_x$ homostructure. (g) Simulated Seebeck signal in $Ti_3C_2T_x$ homostructure changing from S_1 to S_2 in the stacked area (indicated by the dashed line) and the calculated thermovoltage map by convolving with a Gaussian temperature distribution. (h) Linetrace through the $Ti_3C_2T_x$ homostructure (the purple dashed line in the center left in (e)), showing a bipolar thermovoltage signal. (i) Linecut indicated in the center left in (f) by the cyan dashed line, giving a $\Delta S = 1.0 \mu V K^{-1}$.

5.4.2 DC measurements with SThM

The AC technique has some disadvantages, such as a long scanning time on the sample and blurring effects caused by tip movement and the AC heating current. Next, we will develop a direct way to mapping the thermovoltage in MXene devices using a DC method. We fabricated another MXene homostructure device and contacted it with indium needles for SThM DC measurements, as shown in Figure 5.10a. Electrical properties of the device were first investigated. Figure 5.10b presents the linear current-voltage ($I - V$) characterization, showing a low resistance of $\approx 11 \text{ k}\Omega$ measured across the source and drain contacts, which indicates the formation of well-defined homojunctions and good Ohms contacts.

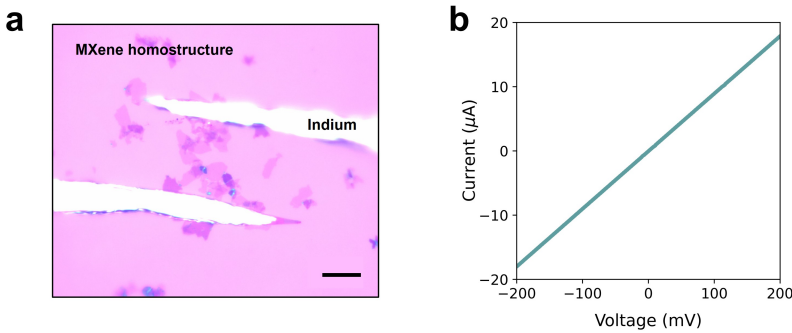


Figure 5.10: (a) Topography and (b) $I - V$ curve of another MXene homostructure device contacted with two parallel indium needles. Scale bar: $10 \mu\text{m}$. This device was used for local DC thermoelectric measurements via SThM.

We mapped the local thermoelectric properties in another MXene device in Figure 5.10 with DC measurements. Compared to one step from monolayer to bilayer ($S_1 \rightarrow S_2$), a bipolar thermovoltage signal was observed across a narrow stacked area ($S_1 \rightarrow S_2 \rightarrow S_1$), as shown in Figure 5.11b. This observed bipolar thermovoltage signal is relatively symmetric because the equal Seebeck coefficient on either

side of the stacked area. The simulation result (Figure 5.11d) also suggests that a bipolar signal is attributed to a peak in the Seebeck coefficient. We extracted the Seebeck change map (Figure 5.11c) and got a $\Delta S = 1.5 \mu V K^{-1}$ (Figure 5.11f). The resulting magnitude and changes in Seebeck of MXene homostructure is similar to the AC measurements.

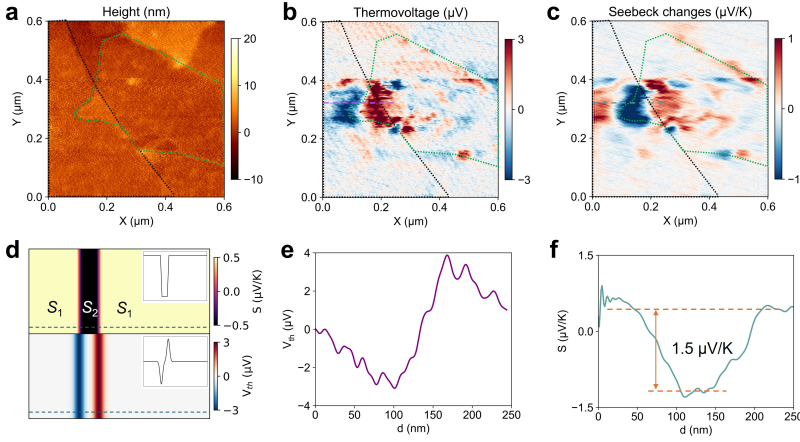


Figure 5.11: (a) Topography, (b) thermovoltage map and (c) extracted Seebeck variation map of the $Ti_3C_2T_x$ homostructure (single flakes were indicated by two dashed lines in different colors). (d) Simulated Seebeck signal in $Ti_3C_2T_x$ homostructure changing from S_1 to S_2 in the stacked area and go back to S_1 (indicated by the dashed line) and the calculated thermovoltage map by convolving with a Gaussian temperature distribution. (e) Linetrace through the $Ti_3C_2T_x$ homostructure (the purple dashed line in the center left in (b)), showing a bipolar thermovoltage signal. (f) Linecut indicated in the center left in (c) by the cyan dashed line, giving a $\Delta S = 1.5 \mu V K^{-1}$.

In addition, thermoelectric puddles were observed along the edges of the single MXene flake (Figure 5.12b), which indicates inhomogeneous Seebeck distributions (Figure 5.12c). This exotic phenomena may be attributed to the combination of strain, defects,

surface terminations, anisotropic nature of the MXene flake, resulting in the local DOS variation in MXene channel and then locally influence the Seebeck coefficient (Figure 5.12f).

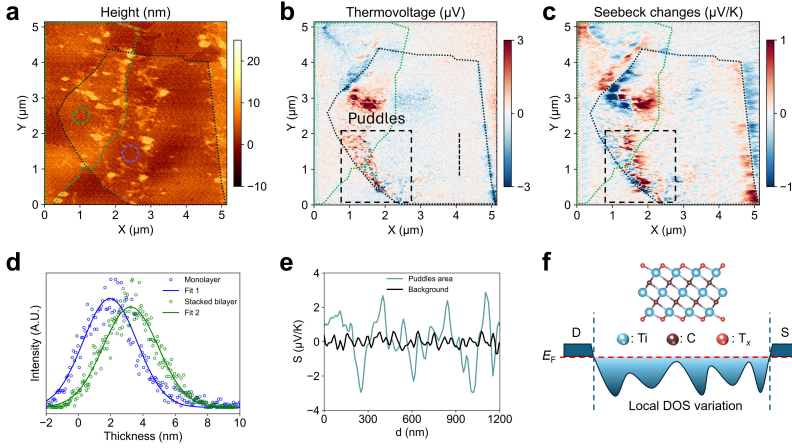


Figure 5.12: (a) Topography, (b) thermovoltage map and (c) extracted Seebeck variation map of the $\text{Ti}_3\text{C}_2\text{T}_x$ homostructure (single flakes were indicated by two dashed lines in different colors). (d) Average thickness in monolayer and stacked bilayer areas (indicated by blue and green circle and fitted with a Gaussian function). (e) Linetrace through the $\text{Ti}_3\text{C}_2\text{T}_x$ homostructure (the cyan and black dashed lines in (b)), showing thermovoltage fluctuations over a short distance. (f) Schematic of local DOS variation of MXene flakes in puddles area which may cause the thermovoltage fluctuations.

5.5 Seebeck coefficient calculation

5.5.1 ΔT calibration of SThM probe

The SThM probe was calibrated in a hot plate to relate the temperature to the electrical resistance of the probe, as shown in chapter 3. We first measured the resistance of the probe as a function of

the bath temperature at different applied power (P_{sthm}). As shown in Figure 3.7, linear regression yields an average conversion factor (the slope) of $15.5 \Omega \text{mW}^{-1}$. We then measured the resistance of the probe as a function of P_{sthm} at different bath temperatures (Figure 3.8). The average slope after the linear fitting is $5.5 \text{ K } \Omega^{-1}$. Combined these two curves, we can obtain the excess Pd heater temperature (ΔT) as a function of P_{sthm} : $\Delta T \text{ (K)} = 85 P_{\text{sthm}} \text{ (mW)}$. That means we can calculate the tip excess temperature by applying the power to the probe. In our experiment, 2 V AC with a 2 V DC offset was used to the probe for DC measurement. Considering our Wheatstone bridge output ratio is 0.1, we get the applied power to the SThM heater P_{sthm} is 0.13 mW, creating a $\Delta T_{\text{dc}} = 11 \text{ K}$. For AC measurement, we used 3 V AC at 57 Hz to the probe and the peak power is 0.26 mW, giving a $\Delta T_{\text{ac}} = 22 \text{ K}$.

When the probe is in contact with the device, it locally heats the MXene flake to generate a sample temperature rise (ΔT_{sample}). We recorded and amplified the open-circuit voltage drop (referred to thermovoltage) as the probe scanned over the sample. It is possible to deconvolute the Seebeck coefficient from the temperature gradient along the sample, as reported elsewhere. But we need to precisely evaluate the temperature gradient and the ΔT_{sample} . As we known, the excess temperature of the probe far away from the sample is ΔT , and it would decrease when touching the sample surface due to the several heat transfer mechanisms (solid conduction, air conduction, water meniscus, et al.) [132].

Because the tip apex temperature ΔT_{tip} also depends on the probe construction (triangular shaped silicon nitride and Pd heater were used in our experiments) and the materials that the tip is in contact with. For the material with high thermal conductivity, gold for example ($310 \text{ W m}^{-1} \text{ K}^{-1}$), ΔT_{tip} would be much lower than the probe temperature ΔT due to the high heat dissipation through the tip-sample contact [50]. To this end, we used COMSOL simulations to estimate the ΔT_{tip} on MXene flake with a low thermal conductivity (A single MXene flake on SiO_2 was defined, the detail

model can be found in Appendix A). Based on the thermal transport measurements in $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in chapter 4, the average in-plane and cross-plane thermal conductivities and the interface conductance were used as the parameters for the simulations. The overall simulated probe and sample surface temperature distributions are shown in Figure 5.13. A ratio of 5.0 was obtained between the probe temperature ΔT and the ΔT_{tip} . The model also takes into account the tip-sample thermal conductance (measured by SThM). When considering all these contributions, we finally extracted the sample temperature rise $\Delta T_{\text{sample}} \approx (1.6 \pm 0.2)$ K for DC measurements and $\Delta T_{\text{sample}} \approx (3.2 \pm 0.3)$ K for AC measurements.

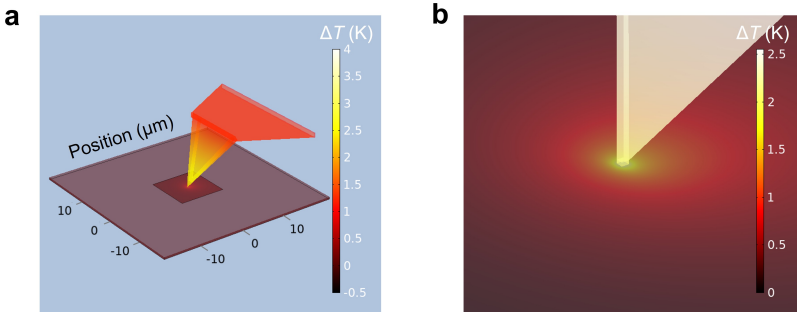


Figure 5.13: SThM tip induced heating simulations. (a) Finite element model for the SThM tip on the SiO_2 -supported MXene flake. (b) Zoom-in view of the model, showing the tip-induced hot spot and the temperature gradient across the MXene flake.

In order to estimate the temperature distribution caused by the hot SThM tip, we fitted the step of thermovoltage at the MXene flake edge (Figure 5.14b) with the sigmoidal Boltzmann curve:

$$f(x) = y_1 + \frac{y_1 - y_2}{1 + e^{\frac{x-x_0}{\Delta x}}} \quad (5.2)$$

This fit gives a $\Delta x = 28$ nm. We then fitted the derivative of the

sigmoidal Boltzmann curve with the below Gaussian function:

$$T(x) = \Delta T_{\text{sample}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \quad (5.3)$$

Where μ and σ is the position of the peak and the standard deviation of the Gaussian distribution, respectively. The fit gives a $\sigma = 45$ nm for Gaussian hot spot from Figure 5.14c and we use it to deconvolute the thermovoltage map to Seebeck variation map (Figure 5.14d). According to the sample temperature rise ΔT_{sample} obtained from the above SThM calibration, we used the resulting Gaussian function to get 2D maps of the assumed temperature distribution (Figure 5.15a) and x -axis temperature gradient ∇T_x (Figure 5.15b).

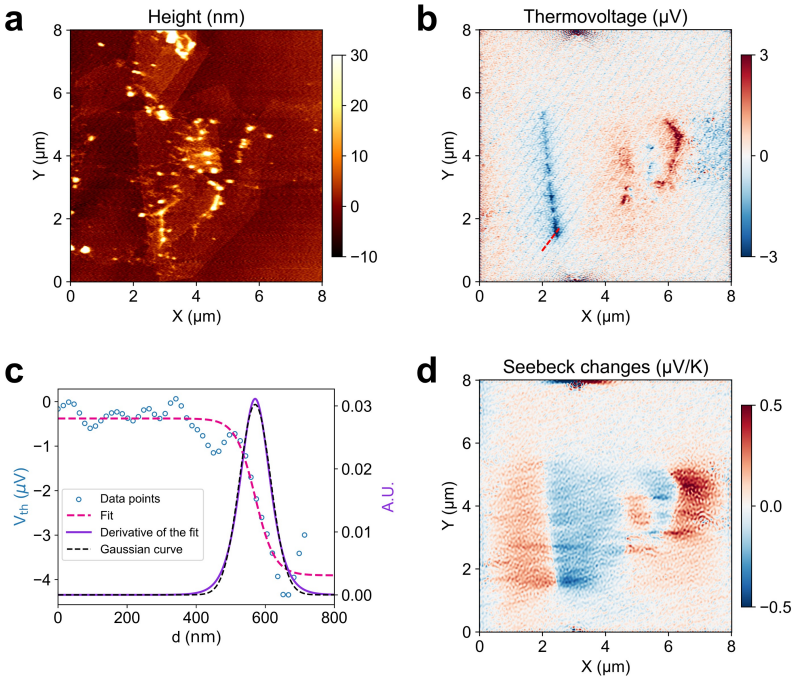


Figure 5.14: (a) Temperature distribution based on a Gaussian function. (b) Temperature gradient with the respect to the x -axis. Insets show the linecuts through the dashed lines.

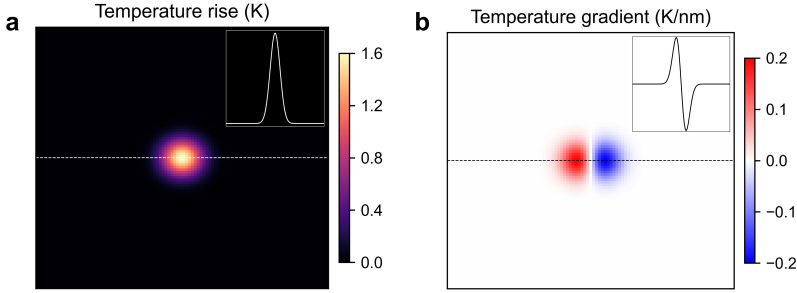


Figure 5.15: Linecut data in Figure 5.14b from substrate to the strong thermovoltage signal area with a sigmoidal Boltzmann curve fit (the pink dashed line) and derivative of the fit.

5.5.2 Estimation of Seebeck variation via pseudo 2D deconvolution

Since $V_{th}(x_T)$ is obtained by the convolution of the ∇T_x and $S(x)$, by knowing the information of ∇T_x (the width and height of the temperature distribution), it's possible to recover complete $S(x)$ maps from a measured thermovoltage by a deconvolution method. In order to access the width of the temperature distribution, we consider fitting a line-cut thermovoltage signal (from no signal in substrate to a strong signal in MXene junction) using a sigmoidal Boltzmann curve (Figure 5.14b). We extracted a $\Delta x \approx 28$ nm, which suggests a spatial resolution of $2\Delta x \approx 56$ nm for the measurement. The width of the temperature distribution was obtained by fitting the derivative with a Gaussian function. We further calculated the 2D maps of the assumed temperature distribution and its temperature gradient based on the resulted Gaussian function. With sufficient knowledge of the temperature distribution induced by the tip, we can deconvolute the thermovoltage signal to extract the Seebeck coefficient variation.

The deconvolution was performed using Pylops package with a L1-regularized filter algorithm to reduce the instabilities of the

inverse process. A 2D FFT filter was used to reduce the wave-shaped noise in DC thermovoltage maps before the deconvolution. We need to figure out the shape of the temperature distribution induced by the tip which is given by the tip apex obtained from thermovoltage maps. We then use the derivative of this Gaussian temperature distribution (temperature gradient) to deconvolute thermovoltage maps and yield the Seebeck coefficient change maps. In the end, a least-squares filter was used to minimize the error between the original and restored image and a Laplacian operator for regularization to enhance the high-frequency features of the image.

However, to perform a pseudo-2D deconvolution, we need to make the following three assumptions: 1) The temperature distribution follows a Gaussian function due to the point heat source feature of the tip; 2) The thermal spreading resistance along the flake is constant and therefore a constant tip-apex temperature $\Delta T_{\text{tip}} \approx 2.2 \text{ K}$ which was extracted from the probe calibration and COMSOL simulations (see Figure 5.13). 3) The thermovoltage signal was measured along x -axis in between two contacts (parallel contacts in Figure 5.2d and Figure 5.10a). The deconvolution is performed line-by-line with the thermovoltage map in the x -direction without any contribution from the y -direction.

We obtained the resulting Seebeck variation maps, shown in Figure 5.9c and 5.9f. It is important to note here that these are not real MXene's Seebeck coefficient maps but rather local Seebeck variation maps. A stepwise change in S between single-layer and bilayer MXene, the $\Delta S = S_{\text{single}} - S_{\text{bilayer}} = 1.0 \mu\text{V K}^{-1}$ (Figure 5.9i) was extracted by a linecut across the homojunction in Figure 5.9c. The value is very close to the one we measured in on-chip thermoelectric devices. We also could see artifacts caused by the changing of tip-sample thermal conductance in the gold contact area. Besides the Seebeck difference along the $\text{Ti}_3\text{C}_2\text{T}_x$ homostructure junctions, we observed a chaotic local thermovoltage variation along the monolayer region (indicated by the dashed black box)

and it differs dramatically over a short distance (Figure 5.12b). This phenomenon has previously been observed in graphene on SiO_2 substrate related to the charge puddles at the Dirac point [50]. Ideally, in a high-quality MXene single flake with uniformly distributed surface terminations (i.e., a constant S in the flake), no thermovoltage signal should be observed when the probe is scanned across the device. However, there is a much stronger thermovoltage variation observed in puddles areas than the noise background (Figure 5.12e). As discussed above, because S is highly related to local band electronic structure of a material. Local factors such as surface terminations, interplays, defects and strains in MXene flakes can influence its local density of states, which causes the Seebeck variations across the flakes. Surface terminations (*e.g.*, $=\text{O}$, $-\text{OH}$, $-\text{F}$) can alter the electronic structure (or DOS) of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene based on the previous theoretical calculations. An O-rich surface shows a lower DOS while OH-rich shows a higher DOS at Fermi level [206]. In addition, theoretical calculations showed that the S of MXene is significantly influenced by the surface terminations [41]. Therefore, one possible interpretation is that the nonuniformly distributed surface terminations (or the different ratio of the surface terminations) cause the local Seebeck symmetry broken across the flake and then lead to a local S change. Since MXene flake tends to oxidize in air and it usually starts from the edge of the flake and propagates inwards. Nanoscale TiO_2 crystalline clusters also grow during the oxidation [207, 208], which leads to local disorders at the edges and Seebeck fluctuation. An evident from STM measurements showed that local variation in surface terminations and TiO_2 clusters yield different work functions and conductance of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene [206]. Local potential variations in monolayer flakes are also observed in KPFM image (Figure 5.7b). These factors can change transport properties locally and would be more obvious along the edges. We actually observed the thermovoltage fluctuations along the edges (Figure 5.12b). The high fluctuations and sign changes in thermovoltage reflect the shift of DOS near the Fermi level. As

discussed above, it's important to note that although thermovoltage is tied to the local DOS of 2D materials, the local phonon scattering in single flakes also plays a role in generating a large change in local temperature (asymmetric distribution) [209], resulting in thermoelectric puddles in the sample surface.

In our experiments, we extracted three key transport parameters: the electrical conductivity, thermal conductivity, and Seebeck coefficient. Using these parameters, We estimated the ZT of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene and obtained a value of 3×10^{-4} for the monolayer. This very low ZT is a record of the low Seebeck coefficient of $\approx 1 \mu\text{V K}^{-1}$ and indicates that pure $\text{Ti}_3\text{C}_2\text{T}_x$ MXene is not an efficient thermoelectric material. However, a low ZT or S can be advantageous in nanoelectronic devices, as it helps eliminate parasitic thermoelectric noise, especially at cryogenic temperatures.

5.6 Conclusion

In this chapter, we experimentally studied the thermoelectric properties of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes via an integrated on-chip heater and the SThM technique. The absolute Seebeck coefficient of a single flake changes significantly with an vertically increasing number of layers. The layer-dependent behavior is primarily attributed to interlayer interactions in MXene layers. Surface terminations may also contribute to these interlayer interactions, leading to significant changes in the band structure and enhanced interfacial scattering, thereby affecting the transport properties. Local thermoelectric mapping further reveals a stepwise Seebeck change at the junction between monolayer and bilayer regions, directly visualizing the interlayer interaction through the local thermovoltage response. Additionally, spatially distributed thermoelectric puddles are observed in MXene flakes, which could be attributed to strain, defects (*e.g.*, wrinkles, TiO_2 clusters), non-uniform surface termination distribution, or potential measurement artifacts. These local features

introduce broader perspective for understanding the thermoelectric behaviors and highlight the importance of nanoscale characterization in fundamental transport properties of MXenes. The layer-dependence thermoelectricity in MXene flake offers insights into its interlayer interactions and may inspire new thermoelectric strategies for designing advanced MXene devices.

Chapter 6

Conclusions and perspectives

This thesis aims at developing a novel high-resolution scanning thermal microscope to locally study thermal and thermoelectric properties in MXenes and the relation to their thickness and local defects. We perform quantitative thermal and thermoelectric measurements on a variety of MXene nanostructures, including monolayer and homostructure devices. SThM is an emerging method to obtain local thermal and thermoelectric parameters, by monitoring the probe-sample thermal exchange process. SThM can thus be employed to extract the local Seebeck coefficient, the local Peltier coefficient or the local thermal conductance of 2D materials. The SThM technique in this thesis is based on the following framework: i) The probe is micro-fabricated Pd-based thermoresistive tip that can be used as both temperature sensor and local heater with a spatial resolution lower than 100 nm. ii) Calibrations are performed for each SThM probe before the thermal and thermoelectric measurements. iii) A constant contact area and thermal contact resistance are assumed when the tip scans over a heterogeneous surface. iv) A statistical method (histogram2d) is used to process the SThM data in order to reduce the impact of artifacts and experimental errors on the

results. v) The temperature distribution induced by the hot tip is assumed to follow a Gaussian profile, and COMSOL simulations are used to estimate the resulting temperature rise in the sample. Therefore, these assumptions underlying the quantitative models are crucial for accurately interpreting the results and understanding the transport properties in MXenes. We will give a summary of the experimental results below.

We use a high-resolution SThM setup with a custom-built bridge circuit, which enables a high signal-to-noise ratio for both AC and DC measurements. Quantitative thermal and thermoelectric characterization of single MXene flakes at the nanoscale were studied for the first time. Firstly, we measure the thickness dependence thermal resistance maps for several kinds of MXenes in chapter 4, including Mo_2CT_x , $\text{Ti}_3\text{C}_2\text{T}_x$ and V_2CT_x . A diffusive thermal transport model is then applied to fit the experimental results. We first study the thermal transport in Mo_2CT_x . However, it is challenging to model the SThM results with an analytical expression, because the high surface roughness of Mo_2CT_x introduced measurement artifacts. Careful probe calibration and precise SThM signal acquisition from high-quality MXene flakes are essential for subsequent quantitative analysis. We then focus on $\text{Ti}_3\text{C}_2\text{T}_x$ MXene and extract its thermal properties from thermal resistance maps, including anisotropic thermal conductivities and thermal interface resistivity with SiO_2 . It is found that $\text{Ti}_3\text{C}_2\text{T}_x$ MXene showed a ultra-low effective thermal conductivity of $0.78 \text{ W m}^{-1} \text{ K}^{-1}$, which is much lower than the value predicted by the WF law. The violation of the WF law may be attributed to the strong electron-phonon interaction. This behavior can decouple the thermal and electrical conductivities of MXenes and offer a new strategy for enhancing their thermoelectric properties. In addition, local thermal resistance variations are observed at defects such as wrinkles and holes in $\text{Ti}_3\text{C}_2\text{T}_x$ and V_2CT_x MXenes.

In chapter 5, we first measure the thermovoltage of $\text{Ti}_3\text{C}_2\text{T}_x$ single flakes using the 2ω method in an on-chip micro-bridge device. It allows us to directly obtain the Seebeck coefficient with high

accuracy. We then realize that the interplay between MXene layers may affect the thermoelectric properties. The layer-dependent thermoelectric properties is further explored by measuring the Seebeck coefficient of $\text{Ti}_3\text{C}_2\text{T}_x$ with different stacked layers. The results show that the Seebeck coefficient changes with the number of layers because of the interlayer interaction, such as interface scattering and band bending. There is evidence from KPFM showing a surface potential difference between monolayer and bilayer $\text{Ti}_3\text{C}_2\text{T}_x$. Compared to the global measurement of the on-chip thermoelectric device, the SThM method is further employed to probe the local thermoelectric response. Both AC and DC approaches are used to map the thermovoltage profiles in $\text{Ti}_3\text{C}_2\text{T}_x$ homostructures. The thermoelectric response reveals the influence of the thickness changes, contacts and local defects on the thermoelectric properties in MXene. In addition, we reconstruct Seebeck variation maps from the experimental thermovoltage maps using the knowledge of the temperature distribution induced by the tip. A Seebeck difference between single and bilayer MXene $\Delta S = 1.0 \mu\text{V K}^{-1}$ is found, which is close to the value measured from the on-chip device.

Thermal and thermoelectric transport measurements can not only provide new strategies to improve material properties but also reveal fundamental physical effects. Especially at the nanoscale, these effects can inform the design of novel devices and advanced applications. For example, it can help to control heat flux in layered materials through interface engineering or anisotropic conduction for thermal management applications. The research also facilitates the development of temperature sensing technologies and energy harvesting systems for self-powered electronic devices.

Additional projects were attempted during this thesis work, but unfortunately could not be fully completed due to time constraints. We will discuss them and present the possible follow-up studies in the following.

Novel SThM systems. This thesis primarily focuses on investigating the thermal and thermoelectric properties of single MXene

flakes using the SThM technique. When measurement is performed under ambient conditions, it is important to take into account the complex heat transfer mechanisms involved. Vacuum operations can increase the thermal resolution by eliminating heat transfer pathways through the water meniscus and air. Therefore, a dedicated vacuum chamber is designed for future SThM experiments. In addition, the parasitic heat by the laser used for AFM feedback (contact mode) may limit the sensitivity of SThM and prohibit the accurate extraction of local thermal conductance values. This is also unsuitable for measuring laser-sensitive materials and devices. Therefore, We can further overcome previous limitations of SThM by developing and fabricating improved SThM probes that are compatible with a tuning-fork AFM (no parasitic laser heating) and a vacuum-SThM system to readily and accurately detect local thermal and thermoelectric signals of devices. Furthermore, the development of a low-temperature SThM setup (<77 K) has not yet been realized. Achieving such low-temperature operation would enable complete thermal and thermoelectric characterization of 2D devices, especially those exhibiting temperature-dependent transport behavior.

Other MXenes beyond $\text{Ti}_3\text{C}_2\text{T}_x$. Some MXenes have been theoretically predicted to be promising candidates for thermoelectric applications, such as Y_2CH_2 ($ZT = 0.97$ and $S = 1188 \mu\text{V K}^{-1}$ [210], Cr_2TiC_2 ($S = 800 \mu\text{V K}^{-1}$ [211]) and Ti_2CO_2 ($S = 1550 \mu\text{V K}^{-1}$ [212]). Although these types of MXenes are challenging to synthesize, further experimental exploration of their thermal and thermoelectric performance is crucial for their practical applications. In addition, surface terminations can significantly influence thermoelectric properties of MXenes. However, synthesizing MXene flakes with only one type of surface groups cannot be achieved using acid etching methods [213]. Kamysbayev et al. reported a molten salt etching method for controlling surface terminations [29]. They successfully synthesized MXenes with single oxygen, imido, sulfur, chlorine, selenium, bromine, and tellurium surface terminations, for example, $\text{Ti}_3\text{C}_2\text{Cl}_2$, $\text{Ti}_3\text{C}_2\text{Br}_2$, $\text{Ti}_3\text{C}_2\text{Te}$, and Nb_2CT_x . By precisely

controlling the surface terminations, we can get a deeper understanding on how these terminations influence heat transport and thermoelectric properties.

Heterostructures or twisted MXenes. 2D vdW heterostructures offer a versatile platform for creating new physics and enable unique functionality. The combination of different 2D materials makes it possible to engineer the electronic, thermal and thermoelectric properties of a device. For example, previous study showed that MoSe₂-WSe₂ heterojunction can be used as a thermal rectifier (or thermal diode) for managing heat flow [36]. We also have shown the possibility to conduct thermoelectric studies in MXene-based heterostructures (*e.g.*, MXene-graphene). We observed the thermovoltage signal along the MXene-graphene junction and the gate-tunable thermoelectric properties can be further investigated. Furthermore, twisted 2D materials can lead to the band structure change, such as flat bands in twisted bilayer graphene [214, 215]. By tuning the angle of stacked layers, it is possible to locally manipulate the thermal conductivity and Seebeck coefficient. For example, the twisted MoS₂ with random interlayer rotations introduce a high thermal anisotropy ratio up to 900 [156]. Some work on probing the local thermovoltage in Moiré superlattice on twisted bilayer graphene has been done using SNOM [133] and SThEM techniques [137]. These approaches provide insights into how twist-induced band structure changes influence thermoelectric properties at the nanoscale. To date, no experimental studies on twisted MXenes have been reported; however, this represents an interesting and unexplored direction that could introduce exotic effects in thermal and thermoelectric transport.

Electrical thermal conductivity. In general, the extracted thermal conductivity from SThM measurement is the total thermal conductivity which is the sum of the electronic contribution κ_e and the phonon contribution κ_{th} . Because most existing techniques for low-dimensional materials are dominated by phonon transport, accessing the κ_e is experimentally challenging due to the prevailing

κ th. Johnson noise thermometry has been employed to isolate and quantify the electronic thermal transport in low-dimensional materials [216, 217]. It is also possible to extract the electronic heat capacity of 2D materials [218]. This method can be further used to probe the electronic thermal conductance of MXenes and investigate strong interaction-driven quantum phenomena.

Appendix

Appendix A: Further experimental details

In this section, we will briefly describe the customized SThM box comprising a modified Wheatstone bridge and a low-noise preamplifier (Figure A.2). The circuit inside the SThM box is shown in Figure A.3. The SThM box components are soldered on a PCB board. Two resistors (R2 and R3) and two capacitors (C1 and C2) are used to balance the bridge. R4 is usually set at the same resistance of the SThM probe, for example 300 to 350 Ω based on the probe we used. In addition, a same-length coaxial cable embedded in the PCB (connecting to R4) is used to match the capacitance of the one connected to the SThM probe. R1 is used to limit the voltage applied to the probe, we usually fix the R1 with a ratio of 0.1. When balancing the bridge, we first adjust the R4 at the resistance of the probe. A small voltage is then applied to the probe to minimize self-heating. We typically use a sinusoidal signal with an amplitude of 0.1 V. Then, R2 and R3 are gradually adjusted (R2 for coarse tuning while R3 for fine tuning) to minimize the bridge output. The capacitors are then tuned, and this process is iteratively repeated to achieve optimal balance. Another advantage of the SThM box is the integration of an ultra-low-noise amplifier, which improves measurement sensitivity by reducing the

electronic noise. It is capable of detecting very low-amplitude signals and variations in dV/V associated with local changes in thermal conductance.

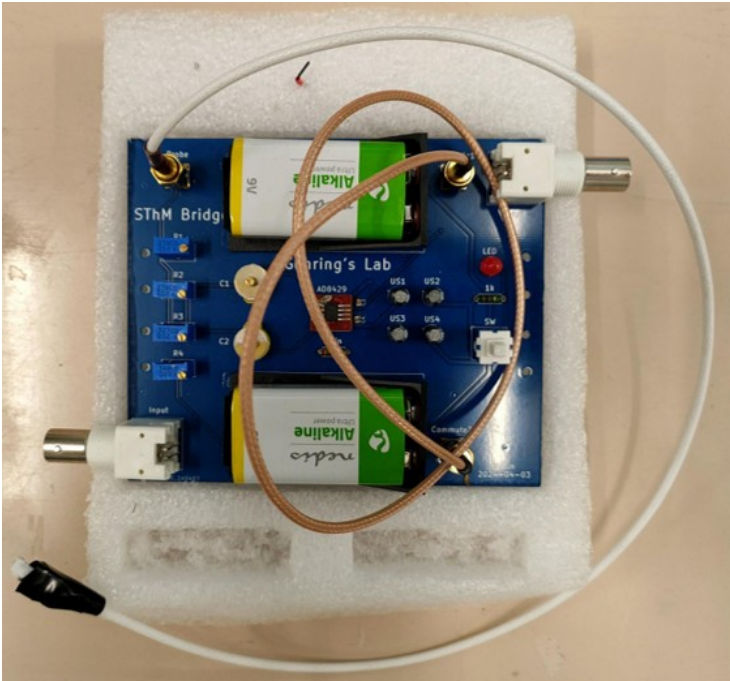


Figure A.1: Optical image of the home-made SThM box with precise amplification.

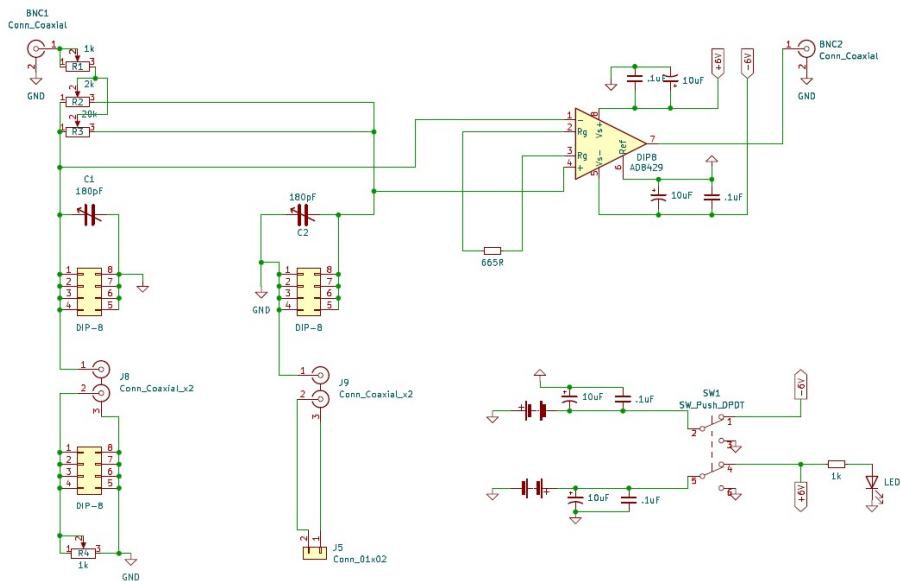


Figure A.2: SThM box circuit with preamplifier.

We measured the thermoelectric properties of MXene flakes with different number of layers via the stamping method. In addition, we made another thermoelectric device with monolayer and stacking bilayer and compared their thermovoltage response, as shown in Figure A.3. The Seebeck coefficient of stacking bilayer MXene is approximately twice that of the monolayer.

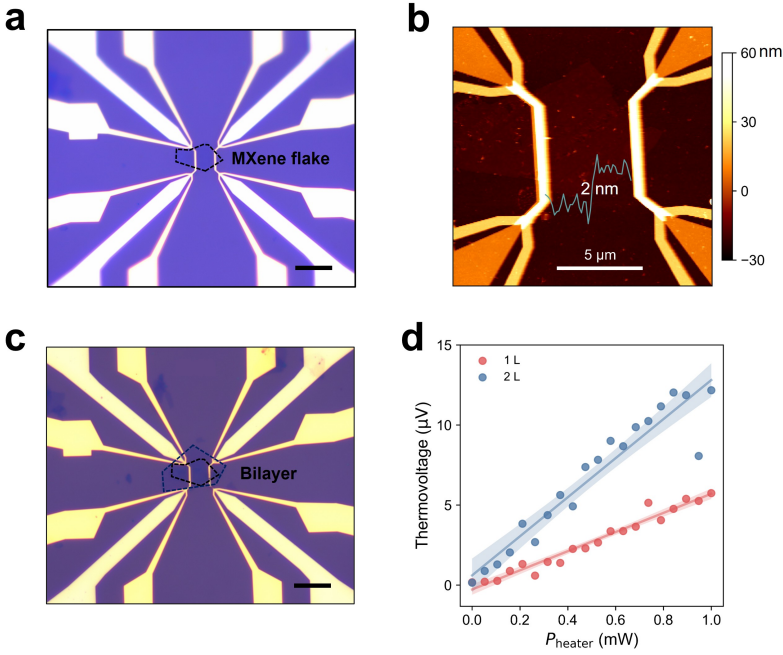


Figure A.3: (a) Optical image and (b) AFM profile of single-layer MXene device. (c) Optical image of bilayer MXene device. (d) Thermovoltage as a function of the heater power for single and bilayer MXene.

COMSOL simulations

We used finite element modelling (COMSOL Multiphysics) to estimate the tip temperature over the supported MXene sample. The model (Figure 5.13a) is constructed of a 290 nm SiO_2 substrate layer with a 2 nm thick $\text{Ti}_3\text{C}_2\text{T}_x$ MXene layer on top. For the SThM probe, its structure is based on the one we used in our experiments. The cantilever is made of Si_3N_4 and a V-shaped thin Pd layer is deposited at the end of the tip. We used measured values for the in-plane and cross-plane MXene thermal conductivities as well as for the MXene- SiO_2 interface thermal conductance. For the substrate interface resistivity, we used $1.0 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$. The power applied to the probe is the same of that of real SThM measurements, which causes Joule heating of the tip. This hot tip is in contact with the MXene layer and a solid-solid heat transfer channel is open. When heat is flowing through the tip apex, the temperature distribution of sample surface changes drastically. Using those material parameters, we modeled the surface temperature distribution and finally obtained the sample temperature rise ΔT_{sample} .

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