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Los Angeles

Structural and Defect Engineering of Electron and Phonon Transport

for High-Performance Electronics

A dissertation submitted in partial satisfaction

of the requirements for the degree

Doctor of Philosophy in Mechanical Engineering

by

Huu Duy Nguyen

2024

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ABSTRACT OF THE DISSERTATION

Structural and Defect Engineering of Electron and Phonon Transport for High-Performance Electronics

by

Huu Duy Nguyen

Doctor of Philosophy in Mechanical Engineering

University of California, Los Angeles, 2024

Professor Yongjie Hu, Chair

The enhancement of modern electronic devices' performance relies on the increased density of electronic components and the miniaturization of device sizes, in line with Moore's Law. However, this improvement often leads to concentrated heat generation within a small area, which can damage the device and limit its performance. Consequently, efficient thermal management has become critically important. My Ph.D. research focuses on the engineering of electron and phonon transport in semiconductors to fine-tune material properties, thereby reducing heat generation and improving thermal management.

My thesis is structured into five main sections. The first section investigates the vacuum field emission properties of tin selenide (SnSe) nanostructures, specifically in the form of 'nano

flowers' (NFs), as an alternative electron transport mechanism that could circumvent the heat generation associated with Joule heating in solid-state devices. The ideal field emission material requires a low work function, high atomic bond energy, and sharp morphological features. SnSe NFs possess these necessary properties. Field emission measurements reveal that SnSe NFs exhibit a high electron emission current density, significant field enhancement factor, and robust emission stability, highlighting their potential for vacuum field emission applications.

The second section delves into phonon transport at the interface between boron arsenide (BAs) and gallium nitride (GaN) to enhance heat dissipation. While GaN is a wide bandgap material favored in high-power and high-voltage devices, such devices demand efficient thermal management for reliable operation. BAs has been identified as a material with superior thermal conductivity, making it a promising candidate for thermal management applications. This study integrates BAs into GaN-based electronic devices to investigate phonon transport across the GaN-BAs interface. The findings indicate a high thermal conductance at this interface, attributable to the good lattice vibration matching between BAs and GaN. Additionally, GaN-on-BAs devices show a substantially reduced hotspot temperature compared to integrated GaN devices with other high thermal conductivity substrates such as diamond or silicon carbide, achieving enhanced heat dissipation and device performance.

The third section examines the controlled doping of van der Waals materials, focusing on black phosphorus (BP). Doping can alter the electron or hole concentration in semiconductors, modifying charge transport properties. However, introducing foreign materials as dopants can also scatter phonons and decrease thermal conductivity. Therefore, precise control over doping is

essential to balance high electrical performance with efficient thermal management. Especially, rational doping control remains challenging for van der Waals structures. This research demonstrates controlled doping of BP, utilizing an electrochemical approach to manage the ion intercalation of lithium and copper. This control transforms pristine black phosphorus-based resistors into n-type and p-type phosphorus-based field-effect transistors, as well as p-n junction diodes, depending on the doping parameters. Furthermore, lithium doping has been shown to enhance charge mobility by reducing neutral impurity scattering. This study proposes a novel method for tailoring the properties of van der Waals materials and provides a new platform for engineering the electron and phonon transport properties of 2D materials.

The fourth section demonstrates dynamic tuning thermal conductivity of tin selenide (SnSe). The manipulation of electricity via logic circuits has been one of the cornerstones of modern technologies. However, manipulating heat through logic units, though equally crucial, has been a longstanding challenge. A primary obstacle is to develop a simple yet effective approach to dynamically tune the thermal conductivity of materials across a broad range, which is vital for optimizing thermal management, enhancing energy harvesting efficiency, and developing thermal logic devices. This study presents a breakthrough in dynamically tuning thermal conductivity via electrical gate-tuning, achieved by modulating electron-phonon interactions in a SnSe thermal transistor. The thermal transistor attained a thermal conductivity tuning. Our analysis based on *ab initio* theory reveals that this modulation in thermal conductivity is primarily stems from the alignment of the SnSe chemical potential with its defect energy level, which activates the electrons of the defect states to scatter phonons. These findings present a novel method for controlling heat flow, opening up new avenues for application in various thermal technologies.

Finally, the fifth section presents thermal properties of defect doped lead selenide (PbSe). PbSe is extensively studied due to its promising thermoelectric properties. Experimental study on the thermal properties of PbSe showed sharpened longitudinal acoustic phonon mode linewidth at high temperature due to reduction of scattering phase space. This study examines the effect of vacancy-induced dislocations on the phonon dynamics of Sb-doped PbSe using inelastic neutron scattering method and diffusivity measurement. The results show sharpening phonon linewidth and enhancement of thermal diffusivity in vacancy-induced dislocations doped PbSe at 300 K. The results show an unexpected impact of defects on the thermal properties of PbSe.

The dissertation of Huu Duy Nguyen is approved.

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2024

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CHAPTER 1. INTRODUCTION

1.1 Motivation and background

In past decades, microelectronic devices such as transistors have scaled in accordance with Moore's Law, which posits that the number of transistors on an integrated circuit doubles approximately every two years. To maintain this pace, the size of transistors has decreased. However, as transistors have become smaller, their heat generation has become concentrated in smaller areas. Currently, the power usage of an integrated circuit is on the order of 100 watts; when converted into power density for the hot spots, this is approximately 1000 watts per square centimeter, which is ten times higher than that of a nuclear reactor core. This high-power density leads to device degradation and diminished performance. Consequently, there is an urgent need for methods to minimize heat generation and for efficient thermal management approaches for future electronics.

To dissipate heat, the conventional method involves conducting it from the device layer into the silicon substrate, then into the environment. However, this may not suffice for future electronics due to the low thermal conductivity of silicon substrates and the high thermal boundary resistance between the device and the substrate. This challenge has motivated my research into engineering electron and phonon transport as a means to reduce heat generation and optimize material properties to fulfill thermal management requirements and enhance the performance of electronics.

1.2 Outline of the dissertation

In this dissertation, I will discuss about strategies to engineering electron and phonon transport for heat management of nanoelectronics. In Ch 2, I will evaluate vacuum field emission property of tin selenide as an alternate electron transport mechanism in order to bypass heat generation due to Joule heating in solid state devices. In Ch 3, I will evaluate heat dissipation capability of boron arsenide as high thermal conductivity substrate material to dissipate heat from solid state gallium nitride-based electronic device. In Ch 4, I will demonstrate ability to control doping of black phosphorus in order to engineer electronic and thermal properties. In Ch 5, I will show thermal conductivity tuning via manipulating electron-phonon interaction of tin selenide sample. In Ch 6, I will present my results on thermal conductivity enhancement of defect doping lead selenide. Finally, I will conclude this dissertation in Ch 7.

CHAPTER 2: FIELD EMISSION BASED ON NANOSTRUCTURED TIN SELENIDE

2.1 Introduction

Solid-state electronics has powered the information technology revolution since the 1960s, however its continuous scaling following the Moore's law is nearing the end due to many intrinsic challenges¹⁻¹⁰. Beyond the traditional metal-oxide-semiconductor field-effect transistors (MOSFETs), advanced design based on new materials and device operations are needed to further improve the speed and performance. Novel 1D and 2D nanomaterials have been the research focus for last decades and enabled new opportunities. Nanowire¹¹⁻¹⁵, carbon nanotube¹⁶⁻¹⁹, and graphene transistors^{20,21} have been intensively studied. In particular, Ge/Si nanowire heterostructure has been created and enabled high-performance transistors significantly outperforming silicon MOSFETs with a 2-THz intrinsic switching speed with a 40 nm channel length device¹¹⁻¹⁵. Other efforts include improving the gate coupling and reducing short-channel effects such as using surrounding gate and FinFETs²²⁻²⁴ as well as developing new operation paradigms such as tunneling transistors²⁵, piezoelectronic transistor²⁶, ferroelectric-gate FET²⁷, spintronics^{13,14,28}, and memristors and neuromorphic devices^{29,30}. These proposed new devices aimed to circumvent intrinsic limitations of MOSFETs and to lower the transistor's power consumption.

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Despite the traditional focus on solid-state electronics, the transport of electrons in vacuum in principle allows for orders of higher velocities and less Joule heating than that in the solid state due to absence of electron and lattice scattering. The high-speed operation is also expected at atmospheric pressure under a small anode-cathode gap below the electron mean free paths in air, which leads to a sufficiently low scattering probability between the electrons and gas molecules. For this motivation, more recently, vacuum field effect transistor (VFET) was proposed as an attractive concept beyond solid-state devices. VFET uses vacuum as its channel instead of the traditional doped silicon channel for charge carrier transport; the electrons travel across the vacuum channel via ballistic field emission to enable high speed. Due to this, VFET is also expected to have high temperature and radiation tolerance; and its operating frequency is expected to be at least ten time higher than traditional MOSFET^{31–33}. In addition, by reducing the channel length below the mean free path of electron in air (~ 100 nm), the VFET can be operational in air due to low probability of electrons and air molecules collision³¹; this effectively removes the high vacuum requirement of the VFET. However, experimental efforts on VFET have been scarce. Silicon-based devices are among the first exploration for VFET due to the ease of fabrication^{34–38}. These early studies show good promise in building nanoscale vacuum devices but also indicate the needs for materials improvement. In particular, the instability and high turn-on voltage of emitter materials present a major challenge. On the other hand, recent literature efforts in studying new materials for field emission provide useful insight. Diamond is one of the most popular materials for field emission application due to its low work function and negative electron affinity, but diamond suffers from high cost, slow growth rates, low quality, and challenging processing with semiconductors. Carbon nanotube, nanowire, and two dimensional materials such as graphene have been studied because of their high aspect ratio and unique nanoscale geometry for

field emission^{39–53}. However, for VFET application, a low turn-on voltage and high stability in air need yet to be demonstrated.

Fundamentally, several merits are needed for the ideal VFET emitter material: First, a low work function is desired for low electron tunneling barrier and thereby introduces a small turn-on voltage. Second, materials with high atomic bond energy are desirable to maintain long-term stable field emission and prevent degradation³⁹. For these required properties, tin selenide (SnSe) seems to be a good candidate for VFET. SnSe is a 2D material with orthorhombic crystal structure, naturally providing a nanoscale field emission tip down to single atomic layer. The bonding energy of SnSe is ~ 4.16 eV⁵⁴, higher than other materials: 3.21 eV for silicon⁵⁴, 2.59 eV for ZnO⁵⁴, and 2.56 eV for MoS₂⁵⁵. The work function of SnSe (3.9 eV)⁵⁶ is also low considering most studied materials. SnSe has been recently studied for thermoelectric applications due to its record-high figure of merit^{57,58}. However, its field emission properties have not been explored so far. Here, we investigated for the first time the field emission performance and stability of SnSe with controlled nanostructure morphologies.

2.2 Tin selenide crystal and tin selenide nanoflower synthesis and characterization

To evaluate the effect of surface morphologies on the field emission performance, we used two different chemical synthesis approaches to control the structures of SnSe in the shape of regular crystals and nanoflowers. First, SnSe single crystals (SCs) with atomically flat crystalline plane surface are prepared via vapor transport method to make a large SnSe crystals. High quality of Sn and Se powder (99.999% purity, from Alfa Aesar) were mixed together and placed into the

quartz tube. The quartz tube is evacuated and flame sealed under high vacuum (10^{-5} torr). We place quartz tube on the multi-zone furnace. Temperature was set the 950 °C and 900 °C as a reaction temperature for hot zone and cold zone, respectively. Temperature of furnace was slowly heated from room temperature to reaction temperature for 12 hours and hold on 96 hours at reaction temperature, and slowly cool down to the room temperature. Sn and Se atoms are covalently bond with ~ 3.1 Å bonding length along the in-plane direction and ~ 2.75 Å along the cross-plane direction⁵⁹; and the layers are weakly bond together by van der Waals force (Figure 2.1a). The as synthesized SC is large but rough (inset of Figure 2.1b) which is not suitable for our experiment; therefore, we mechanically exfoliate the crystal to make a flat surface. The SEM image of the exfoliated SC (Figure 2.1b) reveals the large smooth surface with few broken edges along the in-plane direction of the SnSe crystal.

Second, SnSe nanostructure in the structure of flowers, i.e. nanoflowers (NFs) is synthesized using solution reaction method based on ref⁶⁰. SnSe NF was synthesized by added $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (0.4mmol, 140 mg), SeO_2 (0.4 mmol, 44 mg), and oleylamine (OAM, 20 mL) into a three-neck flask at room temperature. The flask was then sealed and the mixture is stirred continuously for five minutes. Afterwards, the mixture was sonicated for 30 minutes at room temperature. The mixture was degassed with pure N_2 then aged at 150°C for 10 minutes while being stirred continuously under N_2 atmosphere. Finally, the mixture was slowly heated to 350°C at rate $\sim 10^\circ\text{C}/\text{min}$ and aged at 350°C for 15 to 20 minutes. After this process, SnSe NF was extracted and cleaned with excess ethanol. SnSe NF is then dried and stored for following characterizations. In Figure 2.1c, a single piece of NF has been examined by SEM and clearly shows nanoscale sharp tip that could enhance electric field while the whole sample in cm scale (inset, Figure 2.1c) reveals

a dense flower-like morphology⁶⁰ that largely increases surface areas for high power emission with high current density. From the SEM, we estimate the average diameter of a NF particle is around 1.2 μm and the sharp tip is 20~60 nm thick in cross-plane direction and 300~500 nm long in the in-plane direction. Moreover, the SEM images showed the tip of NF is similar to a cylindrical nanowire that enhances field emission. Such a large aspect ratio between the thickness of the tip and the size of NF indicate that the NF-based emitter would strongly improve emission efficiency. We further use atomic force microscopy (AFM) to characterize the exact surface profile of both SC and NF in order to calculate field enhancement factor. The AFM image of the exfoliated SC revealed a flat surface with roughness below 2 nm (Figure 2.1d). The AFM data also shows that the surface profile of a NF tip is plane-like structure with forming an emission tip of about 60 nm thick and 300 nm long (Figure 2.1e). Finally, we use powder X-ray diffraction (XRD) to characterize the crystal lattice structure of our samples. Figure 2.1f shows sharp peaks we observed are corresponding with orthorhombic SnSe with *Pnma* space group #62 (ICDD #00-014-0159) with lattice constants of 11.5 Å, 4.1 Å, and 4.4 Å in a, b, and c direction respectively. In addition, the sharp peaks in Figure 2.1f indicate the good crystallinity of our samples.

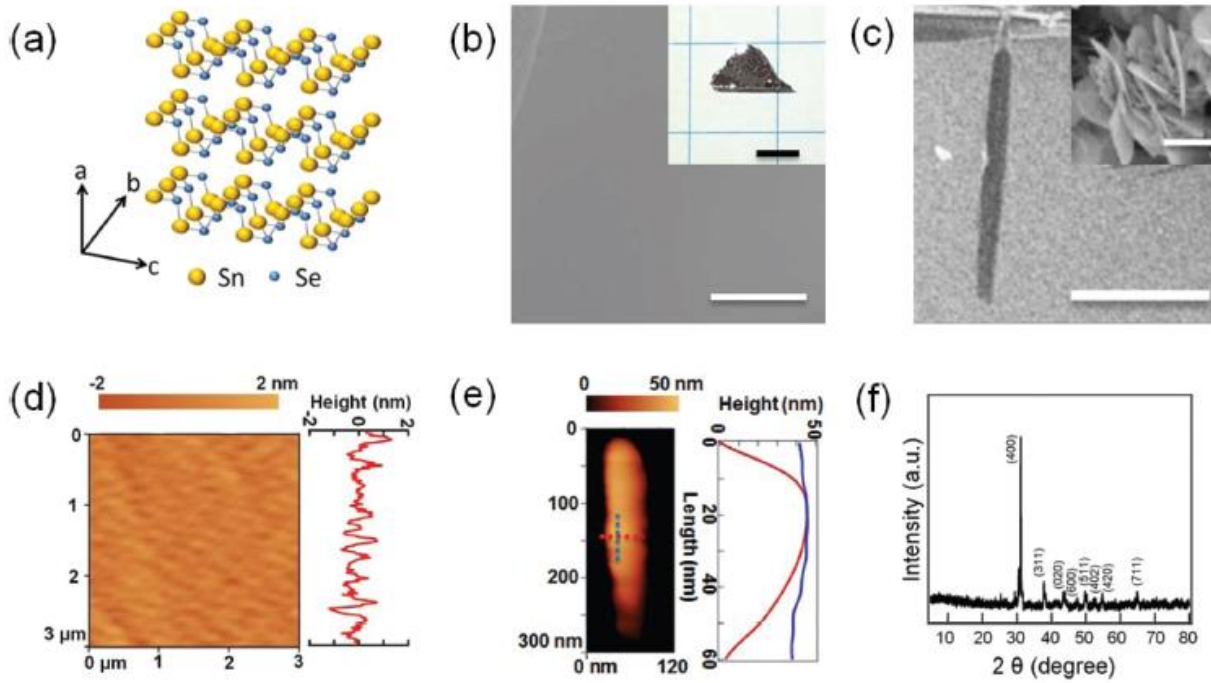


Figure 2.1: Structural design and characterization of tin selenide (SnSe). (a) Schematic illustration of the 2D crystal structure of SnSe. (b) Scanning electron microscopy image (SEM) of an exfoliated SnSe single-crystal (SC) sample; the scale bar is 50 μm . The inset is an optical image of an as-synthesized crystal; the scale bar is 3 mm. (c) SEM image of a single tip of the SnSe nanoflower (NF); the scale bar is 10 μm . The inset is the NF arrays; the scale bar is 500 nm. (d) Atomic force microscopy (AFM) image of the SnSe SC sample. The inset is a one-dimensional surface scan extracted from the AFM image. (e) AFM image along a tip of the SnSe NF. On the right side is the one-dimensional surface profile of the tip, with the red and blue profiles corresponding to the dashed red and blue lines in the AFM image. (f) Powder X-ray diffraction of SnSe.

2.3 Field emission diode fabrication and characterization

Next, to investigate the field emission performance of SnSe, we fabricate field emission devices using the two different SnSe samples as the emitter. The field emission measurement of SnSe is configured in diode configurations as shown in Figure 2.2a. We use oxide insulation layer to control channel length with SnSe as cathode emitter and gold coated glass as anode. To make comparison, we fabricate field emitters based on a single piece of SnSe SC and SnSe NF respectively. SnSe SC cathode was made by exfoliating the crystal to create an atomic smooth surface (top of Figure 2.2a). SnSe NF cathode was fabricated using ebeam lithography and atomic layer deposition (bottom of Figure 2.2a). A gold film was used as the anode for both devices, and was deposited by e-beam evaporation. The channel distance was designed using a thin film of aluminum oxide deposited onto the substrate prepared from ebeam evaporation (middle of Figure 2.2a). This fabrication method effectively creates an 80 μm wide channel with its length controlled by the oxide's thickness. A single field emission device is formed between the gold film and a SnSe SC/NF tip, and its channel length is verified by SEM. As examples show in Figure 2.2b and 2.2c, the channel length between the SnSe and anode is ~ 100 nm which taken as the distance between two flat surfaces (for SC case) and between the apex of the tip of NF and the flat anode. The SEM images reveal smooth surface of SC while the tip of NF is very sharp parabolic tip with many protrusions.

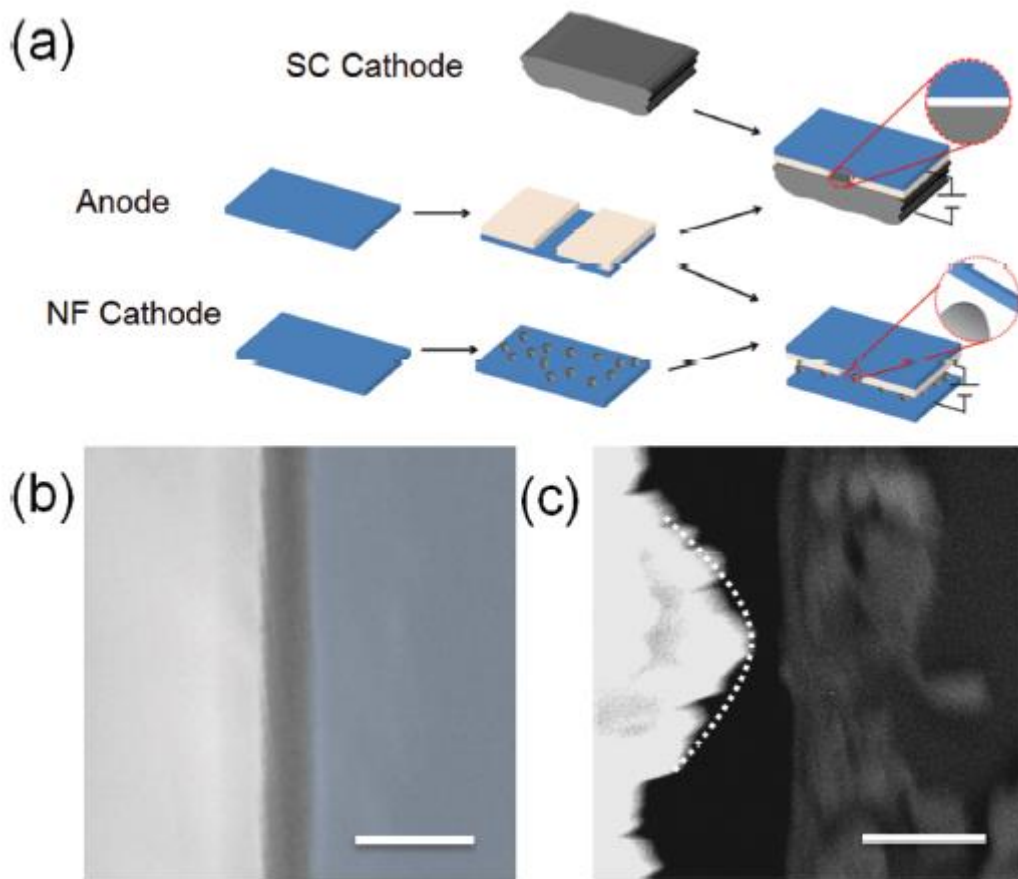


Figure 2.2: Fabrication of SnSe field emission devices. (a) Schematic of the fabrication process. The SnSe emitter, metal collector, and oxide insulation layer are illustrated, respectively, in black, blue, and light pink colors. The fabrication steps are illustrated using the SnSe single crystal (SC) as the emitter (top), gold as the collector (middle), and the SnSe nanoflower (NF) as the emitter (bottom). (b) SEM image of a SnSe SC device with a 100 nm channel. The false color is used to highlight the SnSe SC (white) and the anode (blue). Scale bar, 250 nm. (c) SEM image of a SnSe NF device with a 100 nm channel. The dashed curve illustrates the parabolic profile of a single NF tip. Scale bar, 500 nm.

Next, careful electrical transport measurements were formed on the fabricated devices to evaluate their field emission performance in comparison with other materials and to determine how surface morphology of SC and NF alters the field emission. The samples were measured in air at room temperature and ambient pressure. To initiate field emission we slowly increase the bias DC voltage between the cathode and anode at 0.01 V per increment and record the emission current. The measured field emission J-V curves for SC and NF devices with 100 nm channel are plotted in Figure 2.3a. The field emission curve is similar to that of a diode device as shown in Figure 2.3a: the measured current density is small until the bias voltage reaches a turn-on voltage then it begins to exponentially increase. This is originated from vacuum tunneling which requires that the electrons have enough energy at high bias voltage to tunnel across the vacuum barrier via field emission. In general, the field emission was modeled by Fowler-Nordheim (FN) equation given as

$$I = A \frac{aV^2\beta^2}{h^2\phi} \exp\left(-\frac{b\phi^{1.5}h}{V\beta}\right) \quad (2.1)$$

where A is emitter's effective area, h is vacuum channel length between anode and SnSe cathode emitter through which electron tunnel, ϕ is emitter's work function, β is field enhancement factor which defined as the ratio between local electric field around emitter to the macroscopic applied electric field, and a and b are constant with $a = 1.54 \times 10^{-6} A \cdot eV/V^2$ and $b = 6.83 \times 10^9 eV^{-1.5}Vm^{-1}$. From equation (2.1), it can be seen that the field emission current is largely influenced by the work function, field enhancement factor, and channel length. Therefore, small work function and channel length and large field enhancement factor are needed to achieve large emission current with low turn-on voltage. SnSe NF in Figure 2.3a has higher emission current

density in comparison with SC, which is attributed to the parabolic profile of the NF tip where the local electric field is strongly enhanced versus a flat surface. The turn-on voltage is extracted through the linear extrapolation of the J-V curve. From Figure 2.3a, the turn-on voltage of 100-nm channel NF device is 0.4 V which is significantly lower than literature^{34,35}; we attribute this to the small channel length and the low work function of SnSe.

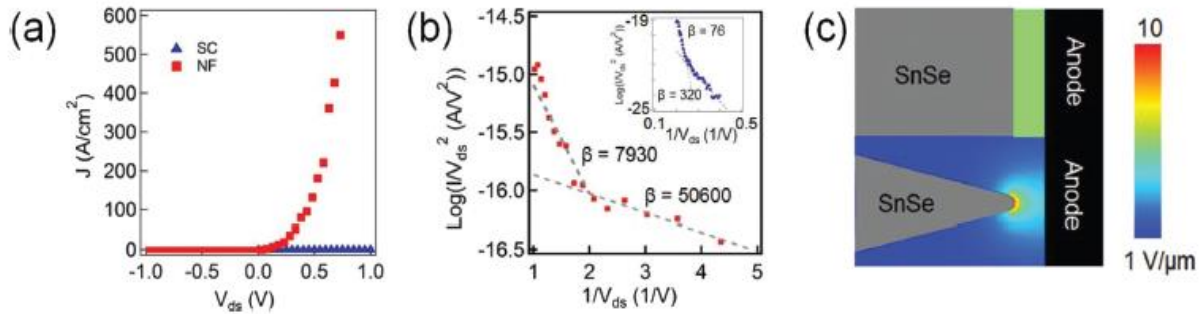


Figure 2.3: Field emission measurement of 100 nm channel SnSe devices. (a) J–V curves of 100 nm channel devices using the SnSe SC (blue) and the NF (red) as the emitter. (b) The Fowler–Nordheim (FN) plot of the SC showed two emission regions. Inset is the FN plot of the NF. The dashed line represents a linear fit of the emission regions. (c) The electrostatic field simulated with COMSOL for the SC (top) and a tip of the NF (bottom).

We replot our emission curve in FN plot ($\log(I/V^2)$ vs. $1/V$) in Figure 2.3b; the prediction lines using FN equation are plotted for comparison, which verifies that field emission is the dominate electron transport mechanism. In Figure 2.3b, the NF yields two straight lines which indicate two different emission regions; and similarly, the FN plot for SC also yields two straight lines (inset of Figure 2.3b). To further evaluate performance on field emission, we extract the key performance metrics of field emission devices, more specifically the field enhancement factor. The field enhancement factor from the slopes of linear regions is evaluated by assuming the channel length h varies with the emitter’s morphology so the FN equation is rewritten as

$$I = \int \int \frac{aV^2\beta^2}{h(x,y)^2\varphi} \exp\left(-\frac{b\varphi^{1.5}h(x,y)}{V\beta}\right) dx dy \quad (2.2)$$

and the slope of straight line in FN plot is then calculate as

$$\frac{d\left(\ln\left(\frac{I}{V^2}\right)\right)}{d\frac{1}{V}} = \frac{d \ln\left(\int \int \frac{\beta^2}{h(x,y)^2} \exp\left(-\frac{b\varphi^{1.5}h(x,y)}{V\beta}\right) dx dy\right)}{d\frac{1}{V}} \quad (2.3)$$

Assuming only single petal tip emit electron (with area of ~60 nm x 300 nm from Figure 2.1e) for NF and an arbitrary area for flat surface, by matching experiment data in Figure 2.3b and morphology of NF tip and SC flat surface, the field enhancement factors of SC are 320 and 76 for first and second regions respectively; and the field enhancement factors of NF are 50600 and 7930 for first and second regions. Interestingly, the field enhancement factor of 50600 measured in NF emitter is record high comparing to the reported literatures with similar channel length⁶¹. The field enhancement factor of SnSe NF is much larger than SC as expected due to its morphology. However, the first region of SC has an unusual large field enhancement factor considering the emitter is a flat surface; the second region has lower field enhancement factor and is more realistic. This phenomenon has been observed for past decades for other emitters^{33,34,62}; the first emission region is most likely originate from the surface roughness we observed in our AFM and SEM measurements (Figure 2.1b and 2.1d) and the second region is originate from the combination of the whole flat surface of SC and the roughness. Likewise, the first emission region of NF with record high field enhancement factor of 50600 is due to protrusions we observed in Figure 2.2c while the second emission region is originate from both protrusions and the NF tip. For 100 nm

devices, the ratio of field enhancement factors between the NF and SC is about 158 and 104 respectively for the two emission regions, indicating that the field enhancement contribution from the surface morphology of NF is about 100 times dominant over that from the channel distances.

The extracted high field enhancement factor is attributed to the unique nanostructures and field emission geometry of the SnSe devices. On the other hand, we note that there are physical and mathematical assumptions for typical FN-type equations, i.e. orthodox emission hypothesis⁶³. In particular, (i) The emitting surface is treated as uniform voltage; (ii) The measured emission current is equal to the device current; (iii) Emission is treated as deep tunneling through a Schottky-Nordheim barrier with quantities independent on the voltage; (iv) The local work function of the emitter is constant. Additional factors may break these hypotheses and introduce non-orthodox. For example: The voltage non-uniformity in the emitting regions and surrounding counter-electrodes for non-metal emitters can likely break the condition (i); Possible scattering or leakage that introduce inequality between emission current and measured device current may break the condition (ii); Dependent variables and barrier-form correction factors in the FN-type equation can break the condition (iii); Local surface trapped charge or defects can result in non-uniform work function of the emitter surface and break the condition (iv). Scaling down the tunneling channel or emitter size may make it even hard to satisfy such orthodox due to more stringent geometric requirements at the nanoscale. Therefore, a more sophisticated data-analysis theory can help better understand the field emission mechanisms for novel materials and nanoscale field emission geometries.

To further study the origin of field emission, we use Finite-Element methods to simulate electric field in SC and NF devices (Figure 2.3c). We model SC as 1 mm thick substrate with a flat surface expose to the anode (top of Figure 2.3c); and for simplicity, NF tip is modeled as 1.2 μm rod with round tip of 60 nm diameter (bottom of Figure 2.3c). We set the gap between SnSe and anode to be 100 nm and 0.5 V bias voltages. The simulation shows that electric field concentrates around the apex of NF tip and gradually decreases along the tip's radial direction; on other hand the electric field of SC is uniform for entire surface. The simulation suggests the NF emits electrons first from the tip's apex due to the concentrated field; and as voltage increases the electric field along the radial direction gradually reaches turn-on field thus begin to emit electron. This reflects in our data in Figure 2.3a in which the emission current is gradually increases with voltage (NF data in Figure 2.3a). For the SC, the simulation suggests that once the turn-on voltage is reached for the flat surface, the entire surface would emit at once. From the simulation, we can clearly see that NF is better emitter than SC purely due to the morphology of the NF that concentrates electrostatic field; however, the NF only emits electron from its tip while SC emits electron from its whole flat surface. Thus, NF has higher field enhancement factor than SC.

We further study the channel length dependence of SnSe NF field emission and determine the distance dependence of turn-on voltage and field enhancement factor. Figure 2.4a shows distance dependence of field emission and Figure 2.4b shows the FN plot of SnSe NF. The extracted field enhancement factor at the second emission region of NF tip for 100 nm, 250 nm, 600 nm, 3 μm , and 6 μm channel are 7930, 5730, 3010, 6190 and 13800 respectively; and the extracted turn-on voltages are 0.40 V, 1.15 V, 2.32 V, 4.44 V, and 9.87 V respectively. Figure 2.4a

and 2.4b show that as channel length increases the turn-on voltage is increases due to more voltage required to maintain same electric field.

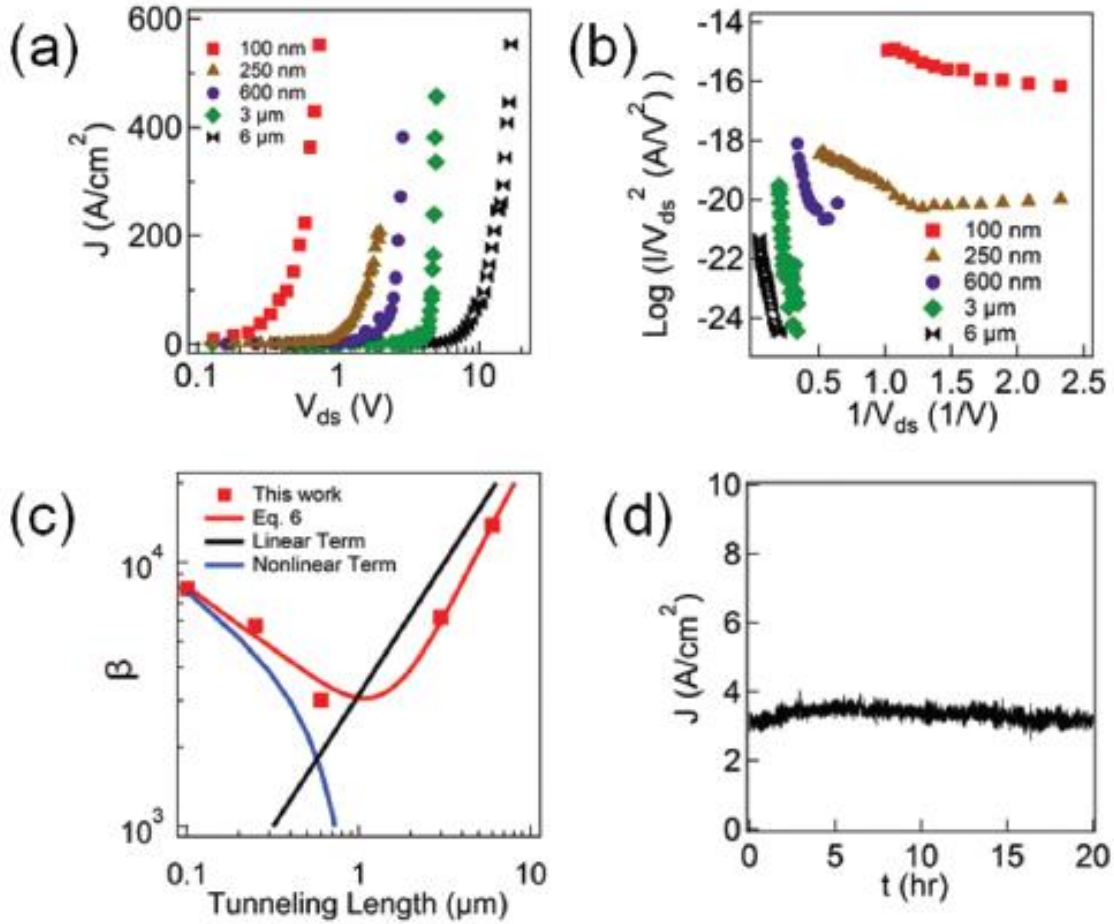


Figure 2.4: Field emission measurement of SnSe nanoflower (NF) devices with channel length scaling. (a) Field emission J - V data of SnSe NF devices with a channel with length from 6 μm to 100 nm. (b) The Fowler–Nordheim plot of the measured field emission of SnSe NF devices with different channel lengths. (c) Field enhancement factor (β) from the measurement (red dot) and empirical fitting (red line) as a function of the channel length. The contribution of linear and non-linear terms in eqn (6) are plotted in black and blue lines, respectively. (d) Emission stability over 20 hours at 3 A cm⁻² for the 100 nm channel SnSe NF device.

We also noticed that the non-monochronic channel length dependence of field enhancement factor is observed in our measurement (Figure 2.4c). The decreases and then increases of field enhancement factor with channel length cannot be simply described using the increasing field enhancement factor at large channel length^{64–69}; however, such behavior has been observed in literature for field emission devices with extremely small channels^{70–74}. The increases of field enhancement factor at small channel length is due to the local electric field at the tip's apex reaches infinity as the channel length approach zero while the macroscopic electric field far away from the tip reaches a finite value. To qualitatively understand this trend, we consider the empirical field enhancement factor for large channel length greater than few micrometers as^{65,68}

$$\beta = Ch + C_0 \quad (2.4)$$

where h is channel length and C and C_0 are fitting constants. With small channel length less than one micrometer, Edgcombe and Valdre modelled the field enhancement factor as^{73,75}

$$\beta = \beta_0 \left\{ 1 + A \left(\frac{h+l}{h} \right) - B \left(\frac{h}{h+l} \right) \right\} \quad (2.5)$$

where β_0 is geometry dependence field enhancement factor, l is height of the emitter, and A and B are fitting constants. As mentioned, the equation (2.4) and (2.5) are inconsistent with one another; to make the equations consistent, we combine the two equations as

$$\beta = \left\{ C_1 + C_2 \left(\frac{h+l}{h} \right) - C_3 \left(\frac{h}{h+l} \right) \right\} + C_4 h \quad (2.6)$$

In equation (2.6), we use fitting constant C_1 instead of β_0 because there is not any theoretical work we aware of to predict the field enhancement factor of NF. We use 1.2 μm as our l ; and 4894, 291, 12383, and 3164 as our C_1 , C_2 , C_3 , and C_4 respectively to fit equation (2.6) fairly well with our data (Figure 2.4c). As shown in Figure 2.4c, at large channel length, the linear term dominates and field enhancement factor varies linearly with channel length (black line in Figure 2.4c); and at small channel length, the non-linear term dominates (blue curve in Figure 2.4c). The transition point appears when channel length is comparable with emitter's length. Physically, as channel length decreases from large channel length, the enhancement factor linearly decreases because the emission geometry approaches plane to plane geometry. However, at the transition point, the local electric field around the tip increases faster than the macroscopic electric field far away from the tip; thus, the field enhancement factor increases. Therefore, in this region, the field enhancement factor is the combination of the decreases of field enhancement factor due to plane-to-plane transition and the increase of field enhancement factor due to rapid increase of local electric field. Interestingly, field emission still happens in air with 6 μm channel; we try to measure field emission stability with large channel length but the current quickly decays. This result is well expected since the channel length is above mean free path of electron in air ($\sim 200\text{ nm}$)³¹. We do not think the reason for current decay is from air ionization since our operate voltage is much smaller than the required breakdown voltages^{76–78}. Thus, the current decay is most likely from electrons scatter with air molecule. We also measure emission stability using the 100 nm channel length and observe more stable emission current (Figure 2.4d). The emission is stable at 3 A/cm² for 20 hours with less than $\pm 5\%$ fluctuations; in comparison, carbon nanotube, MoS₂, and graphene emitters usually have fluctuation on order of $\pm 10\%$ for three hours under high vacuum^{49,79,80}. We attribute the higher stability of SnSe to small channel length and high bond energy of

SnSe. Finally, we compare the performance of SnSe NF with other materials and notice that the SnSe NF devices require lower turn-on voltage (Figure 2.5a). The reduced turn-on voltage for field emission is due to its intrinsic low work function and high surface-enhanced electrostatic field (Figure 2.5b), thus provide advantage for small power operations.

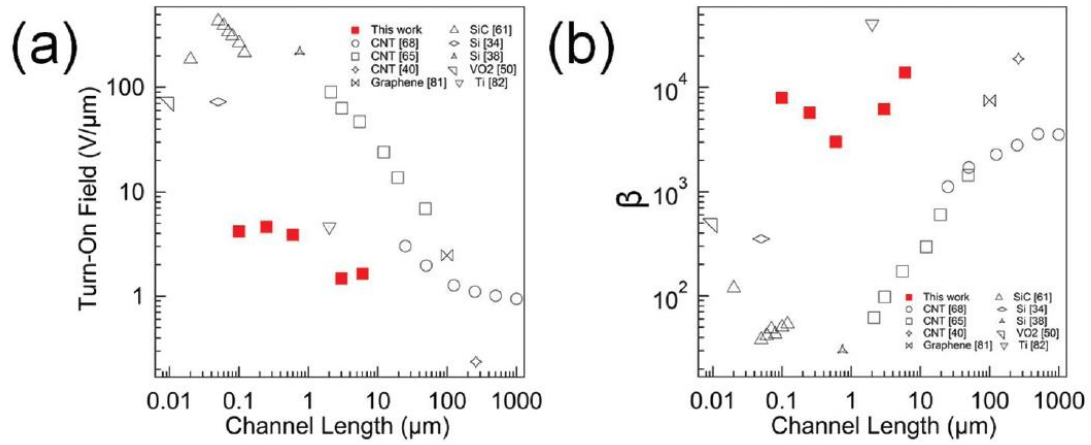


Figure 2.5: Performance comparison between this work and the reported literature studies. (a) The turn-on fields and (b) the field enhancement factors of SnSe devices are plotted with channel length dependence, in comparison with the data from literature studies.

2.4 Summary

In Summary, we demonstrate high-performance and stable field emission of single SnSe nanostructures in air. With the device channel down to 100 nm, we studied field emission from different surface morphology and observed a significant performance improvement of nanoflower surfaces due to the high aspect ratio. Moreover, the SnSe NF requires only 0.5 V bias voltages to facilitate field emission which is lower than most reported works; and such low turn-on voltage is desirable for low power applications. We further investigate the emission of SnSe NF with different channel lengths and conclude the non-monochronic channel length dependence of the

field enhancement factor is due to the rapid increase of local electric field at the tip of SnSe NF as the channel length decreases. Our results show that SnSe nanostructured is a promising material for vacuum field emission and underscores the promise of rational materials design at the nanoscale to develop new building blocks beyond conventional electronics.

CHAPTER 3: INTERFACE PHONON TRANSPORT: BORON ARSENIDE COOLING SUBSTRATE FOR GALLIUM NITRIDE

3.1 Introduction

In most electronic systems, large amounts of waste heat are dissipated from hot spots to heat sinks across a series of device layers and interfaces that have a thermal resistance. A large thermal resistance—and hence rising hot-spot temperatures—can degrade device operation, so thermal management is an important technological challenge in the semiconductor industry^{1,2,81}. Recent research on improving heat dissipation has focused on replacing common substrates (such as silicon carbide, silicon and sapphire) with high-thermal-conductivity (HTC) materials to reduce the overall thermal resistance^{3,82–88}. A key challenge for high-performance thermal management is to achieve the combination of HTC with a low thermal boundary resistance (TBR—the resistance of an interface to thermal flow) near electronics junctions².

Diamond is currently the leading research prototype HTC material for high-performance power electronics cooling. It has been studied with wide-bandgap semiconductors and shown reduced hot-spot temperatures in gallium nitride (GaN)–diamond devices compared with traditional radiofrequency (RF) systems. However, GaN–diamond interfaces have poor TBR, which compromises the application potential of diamond for thermal management^{2,3}. Conventional

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HTC materials have also been limited by their thermal properties and other intrinsic issues. For example, diamond and cubic boron nitride are challenging for applications because of their high-temperature and high-pressure synthesis requirements, slow growth rate, high cost, degraded quality and difficulty integrating with semiconductors. Graphite is highly anisotropic and mechanically soft due to having weak cross-plane van der Waals bonding. Nanomaterials such as graphene and nanotubes can be good conductors for individual materials, but, when integrated at practical sizes, their thermal conductivity degrades due to ambient interactions and disorder scattering.

Recently, new compound semiconductors^{3,85–88} have been developed experimentally based on ab initio theory^{89–97} and exhibit high thermal conductivity beyond that of most common heat conductors. In particular, an isotropic thermal conductivity of $1,300 \text{ W m}^{-1} \text{ K}^{-1}$ has been reported in boron arsenide (BAs^{3,88}). BAs has a thermal conductivity over three times that of industrial HTC standards such as copper and silicon carbide (SiC)—both around $400 \text{ W m}^{-1} \text{ K}^{-1}$ —and twice that of cubic boron nitride. Furthermore, the mechanical and thermophysical properties of BAs have been measured to be highly compatible with power semiconductors⁸⁸, as desired for device integration. The heterogeneous integration and characterization of BAs with other material layers is critical to achieving their future implementation in devices for thermal management applications, but these remain unexplored.

In this chapter, we report the interface characterization and integration of BAs with other metal and semiconductor materials. We examine the heat dissipation performance and mechanisms at these interfaces via material characterizations, spectroscopy measurements and atomistic

phonon transport theory simulations. Because of the unique phonon band structures, BAs shows a combination of high HTC and low TBR. Here, we develop GaN-on-BAs structures using metamorphic heteroepitaxy and measure a thermal boundary conductance of $250 \text{ MW m}^{-2} \text{ K}^{-1}$. In the following, we highlight the potential of BAs as an alternative cooling substrate to diamond and other state-of-the-art HTC materials by using experimental data from GaN–BAs structures with a variable-width heat source to determine and investigate hot-spot temperatures of GaN transistors as a function of length scaling (from $100 \mu\text{m}$ to 100 nm) in both diffusive and ballistic transport regimes. We also develop device integration and provide experimental measurements of operational AlGaIn/GaN high-electron-mobility transistors (HEMTs), verifying the superior cooling performance of BAs and showing its substantially lower hot-spot temperature ($\sim 60 \text{ K}$) than diamond ($\sim 110 \text{ K}$) and SiC ($\sim 140 \text{ K}$) at the same transistor power density.

3.2 Minimize Thermal Boundary Resistance by Minimize Debye Temperature Difference

TBR is limited by the scattering of energy carriers from both sides of the interface^{82,98,99} and has been shown to exist at all heterogeneous interfaces, regardless of atomic perfection. Despite improvements in material quality, such as surface roughness and defects^{82,100}, the ultimate limit of TBR for semiconductor device interfaces is usually dominated by the mismatch of atomistic vibrations (the modes of which are defined as phonons⁹⁸) across the interface (Figure 3.1a). Under the classical Debye approximation, the vibrational properties of materials are approximated by linear phonon dispersion, and the maximum temperature of the highest phonon frequency is defined as the Debye temperature (Θ_D)¹⁰¹. A simple metric to qualitatively evaluate the overlap between phonon spectra of two materials is to compare

their Θ_D values⁹⁹, where a smaller difference in Θ_D across the interface will be expected to result in a smaller TBR. Figure 3.1b compares Θ_D values for typical semiconductors, metals and HTC materials. Most semiconductors (such as silicon, germanium, GaAs and GaN) and metals have Θ_D values below 700 K, while prototype HTC materials such as diamond and cubic BN have much higher values of Θ_D (over 2,000 K) due to their large phonon group velocity. It is therefore expected, and studies have confirmed, that there is a large TBR for diamond and BN interfaces after integration with typical semiconductors, which substantially compromises their application potential for thermal management, despite their high thermal conductivities. For example, the interface between diamond and GaN has a mismatch in Θ_D of over 1,500 K, resulting in a TBR of $\sim 30 \text{ m}^2 \text{ K GW}^{-1}$ (refs.^{102–104}). By comparison, BAs has much lower Θ_D values (for example, BAs has a Θ_D of $\sim 700 \text{ K}$), suggesting they may show improved TBR upon integration.

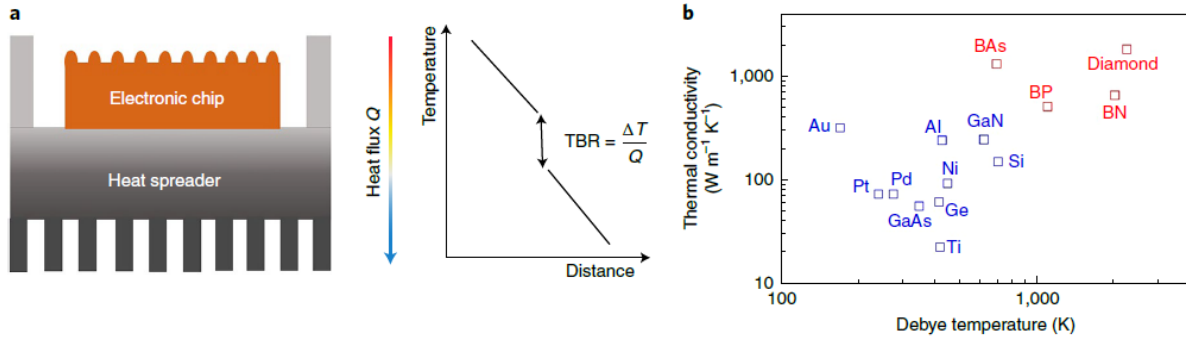


Figure 3.1: Electronics thermal management using integrated HTC materials as a cooling substrate to improve heat dissipation. (a) Schematic illustrating heat dissipation and thermal boundary resistance (TBR) at the interfaces in microchip packaging. $\text{TBR} = \Delta T/Q$, where ΔT and Q are the temperature drop and heat flux across the interface, respectively. (b) Room-temperature thermal conductivities and Debye temperatures of representative metals, semiconductors and HTC materials.

Thermal transport was measured using ultrafast pump–probe spectroscopy based on the time-domain thermoreflectance (TDTR) technique, as illustrated in Figure 3.2a. TDTR is well suited for this, as it requires no physical contact with the sample and the measurement can determine the TBR precisely^{3,100,105,106}. In our set-up, a femtosecond-pulse laser with repetition rate of 80 MHz is generated by a Ti:sapphire optical cavity and divided into pump and probe beams. The pump beam doubles its frequency (a wavelength of 400 nm) after passing through a second harmonic generator, and is used to thermally excite the sample surface. The probe beam, at a wavelength of 800 nm, is used to detect the sample temperature. The time delay between pump and probe beams is precisely controlled by a mechanical delay stage with subpicosecond resolution. To determine the TBR, the transient TDTR signal is detected and fitted to a multilayer thermal model (Figure 3.2c).

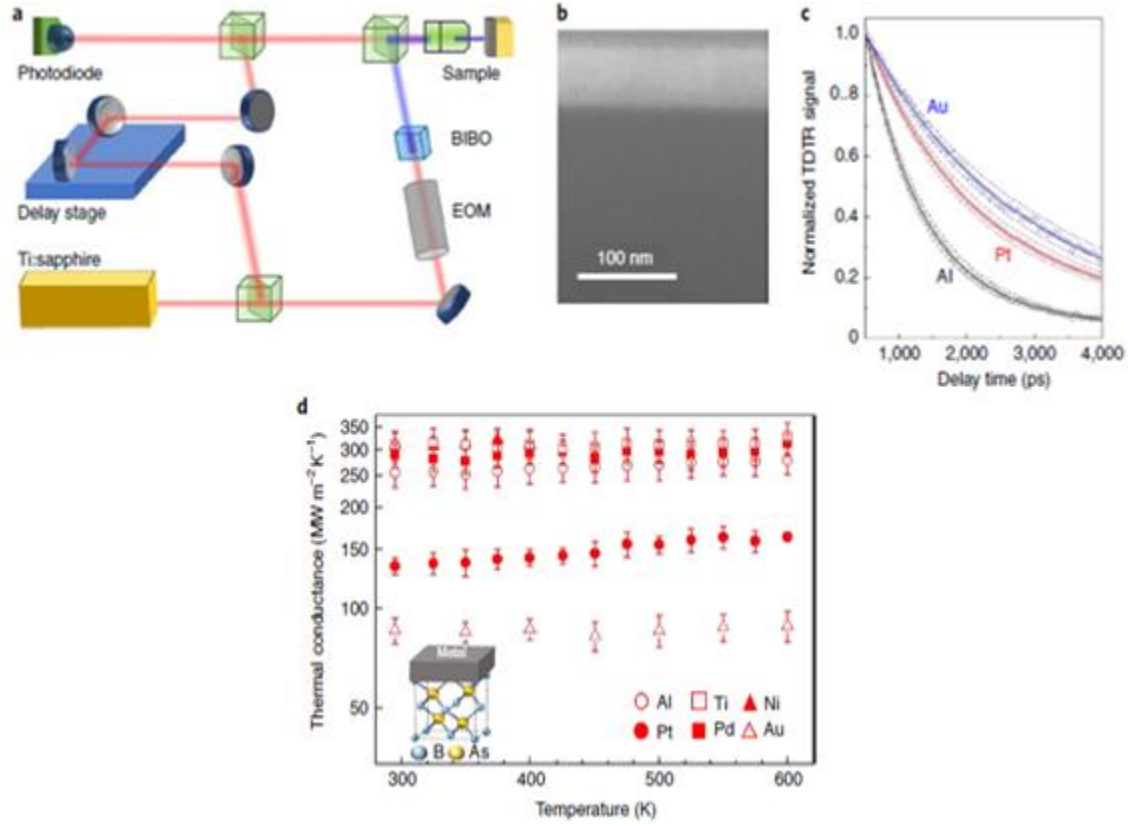


Figure 3.2: Heterogeneous interfaces and ultrafast optical spectroscopy measurements of temperature-dependent thermal boundary conductance. (a) Schematic of the TDTR measurement set-up. Blue and orange routes represent pump and probe laser beams, respectively. EOM, electro-optic modulator; BIBO, bismuth borate. (b) BAs and BP act as a cooling substrate for metal films. A cross-sectional SEM image of a typical sample is shown. The top layer is aluminium film and the bottom layer is BAs. (c), Typical TDTR experimental data versus time (open circles), fitted to the thermal transport model (solid lines). Calculated curves (dashed lines) are shown with the thermal boundary conductance changed by $\pm 10\%$ of the best values to illustrate measurement accuracy. (d) Experimental results for the temperature-dependent thermal boundary conductance between a range of metals and BAs. Error bars indicate the standard deviations of measurements.

First, we measured the thermal transport across the interfaces of BAs with various metals. Aluminum, gold, nickel, palladium, platinum and titanium films were deposited on top of BAs thin films by electron-beam evaporation to form a clean metal–HTC interface, as verified by cross-sectional scanning electron microscopy (SEM; Figure 3.2b). Our measurements of the temperature-dependent thermal boundary conductance (G , the reciprocal value of TBR) are shown in Figure 3.2d. In general, metal interfaces with BAs are measured to have high thermal conductance. The value of G varies for each metal but has a similar trend for BAs. For example, gold and titanium have the lowest and highest G values, respectively. The measured thermal boundary conductance values (at room temperature) between BAs and gold, platinum, aluminum, palladium, nickel and titanium are 85, 133, 250, 290, 309 and 310 MW m⁻² K⁻¹, respectively. The thermal boundary conductances of BAs with metals are typically over 4× higher than those of a metal–diamond interface¹⁰⁷, verifying their high heat dissipation efficiency.

3.3 Heterogeneous Integration of Gallium Nitride and Boron Arsenide

We next demonstrate the experimental integration of BAs with a prototype high-power semiconductor, GaN, and measure the heat dissipation performance. Recent progress^{102–104,108–112} has been made in integrating GaN with classical HTC materials (in particular, diamond and SiC) for power cooling, with a focus on improving the near-junction lattice mismatch, defects and the resulting TBR (which limits the overall heat dissipation). To directly integrate BAs with GaN is challenging, because the crystal structures of BAs (zinc blende cubic) and GaN (wurtzite) are different, making it difficult to form epitaxial interfaces with minimum disorder. Also, BAs decomposes at ~1,200 K, so low-temperature crystal growth is required. To obtain a high-quality

interface between BAs and GaN, a metamorphic heteroepitaxy method was thus used to relax the strain¹¹³, with a thin layer of oxide introduced between them as an adhesion layer, using an atomic layer deposition technique¹¹⁴. In short, a GaN-on-Si wafer consisting of an $\sim 1\text{-}\mu\text{m}$ -thick AlGaIn transition layer, $1\text{-}\mu\text{m}$ -thick GaN buffer layer and 20-nm AlGaIn top barrier layer was used as the device layer. The Si substrate and AlGaIn epitaxial transition layer, used to accommodate the lattice mismatch during GaN-on-Si growth, were selectively etched out using an $\text{HNO}_3\text{:HF:CH}_3\text{COOH}$ (5:4:1) mixture and AZ400K developer, respectively. This resulted in clean and smooth GaN surface. A thin oxide layer was deposited on each surface of the BAs and GaN samples using atomic layer deposition (Fiji F200, Cambridge Nanotech). Trimethylaluminum was used as precursor to deposit 10 cycles of Al_2O_3 at 473 K. Oxygen plasma treatment was applied to the oxide layers. BAs and GaN samples were mechanically transferred and bonded together via the oxide layers. The bonded BAs–GaN samples were annealed at 773 K in vacuum to form the high-quality interfaces for measurements.

The heterogeneous interface was verified by SEM and high-resolution transmission electron microscopy (HR-TEM). Figure 3.3a shows an atomically clean and uniform GaN–BAs interface with a 2-nm interlayer aluminum oxide. The thermal boundary conductance of the high-quality BAs–GaN interface was measured using TDTR as $\sim 250\text{ MW m}^{-2}\text{ K}^{-1}$, which is over eight times higher than that of typical GaN–diamond interfaces^{102–104}. Moreover, considering that the oxide layer could serve as a barrier to scatter phonons and introduce an additional series resistance ($\sim 1.4\text{ m}^2\text{ K GW}^{-1}$ for 2-nm oxide, or 35% of the measured total resistance), the TBR of the GaN–BAs interface could be subject to further enhancement through optimization of the resistance contribution from the oxide interlayer.

To evaluate the device-level heat dissipation performance of BAs as a cooling substrate, we determined the hot-spot temperature across a GaN–BAs interface as a function of various heating sizes from 100 μm to 100 nm (Figure 3.3b). The heat dissipation performance of the GaN–BAs device was compared with that of a current state-of-the-art GaN–diamond device. We considered an example device geometry involving a GaN device layer on top of a BAs or diamond cooling substrate by using experimental data as the input and solving the heat conduction equation and the Boltzmann transport equation (BTE; top right inset, Figure 3.3b). A boundary line heat source with fixed power (for example, 10 W mm^{-1}) was placed on top of the GaN layer to serve as the hot spot, and the bottom of the substrate was fixed at room temperature. To study the size-dependent effect of the hot-spot temperature, the width of the heat source was varied. Experimental data for the TBR and thermal conductivity were used for these simulations.

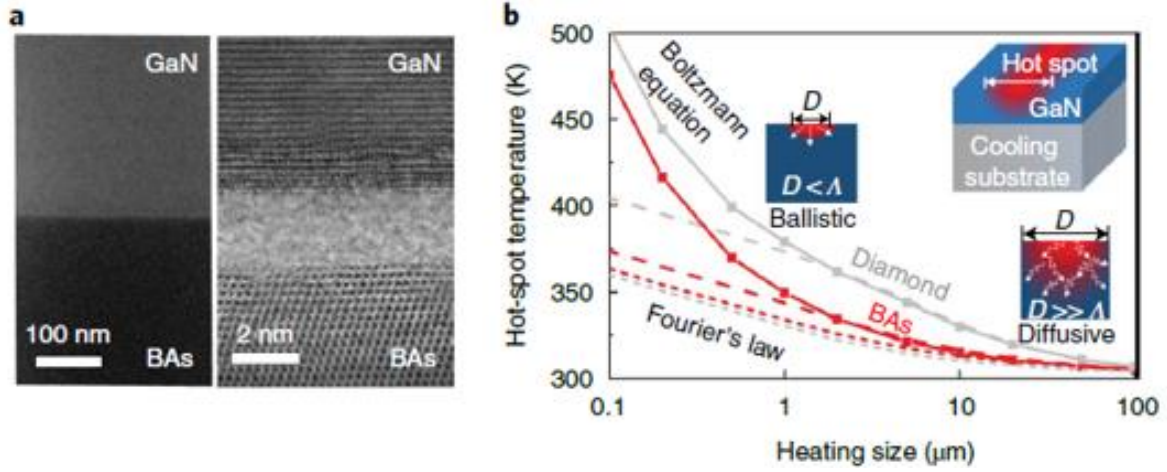


Figure 3.3: Device integration of BAs and GaN for high-performance thermal management versus transistor channel length scaling and power density. (a) Cross-sectional SEM (left) and high-resolution TEM (right) images of a GaN–BAs structure, showing the atomically resolved interface. (b) Simulations of the hot-spot temperatures for the two best thermal conductors (BAs and diamond), as a function of heating size (from 100 μm to 100 nm). Top right inset: schematics of transport physics and the simulation domain, including a 0.8- μm -thick GaN layer on top of a 100- μm -thick cooling substrate. All simulation inputs are from experimental measurements and ab initio calculations. A comparison of Fourier’s heat conduction law (dashed lines) and the spectral-dependent Boltzmann transport equation (solid lines) quantifies the transition from diffusive to ballistic thermal transport (smaller insets). The size-dependent hot-spot temperature results indicate that BAs has a superior performance for nanoscale thermal management due to both its high thermal conductivity and thermal boundary conductance.

We first simulated a hot-spot temperature by solving the heat conduction equation using the finite-element method. In this case, thermal transport is considered as a diffusive process, where the heat flux is proportional to the temperature gradient (following Fourier’s heat conduction law). Classical diffusion theory describes the thermal transport process well when the

characteristic length is far larger than the phonon mean free path, and is commonly used for engineering macroscopic devices. The hot-spot temperature increases when the heater width decreases, due to the larger heating power density. To evaluate the effect from TBR, by intentionally removing TBR in the simulation (dotted lines), we found that, as expected due to its high thermal conductivity, diamond shows a slight advantage. However, when TBR is included in the simulation (dashed lines), which is the case for practical devices, BAs has a much lower hot-spot temperature than diamond, supporting its superior performance in heat dissipation through the combination of a high HTC and low TBR.

We also evaluated the device performance under conditions where ballistic transport takes place and classical diffusion theory fails for nanoscale devices⁹⁷. On shrinking device sizes below the phonon mean free paths, phonon transport will not experience scattering. In this case, practical heat dissipation behaves more like radiation than diffusion, so the actual hot-spot temperature will deviate from the prediction of Fourier's law. The ballistic thermal transport and phonon mean free path spectra of GaN, diamond, BAs and BP have all been experimentally measured and analyzed in our recent studies^{3,85,97}. Here, to capture the physics of thermal transport from the diffusive regime to the ballistic regime, we solved the spectral-dependent BTE considering mode-dependent phonon properties for the same device structure. The three-dimensional (3D) spectral-dependent BTE is given by

$$\frac{\partial f}{\partial t} + \mathbf{v}(\omega, i) \cdot \nabla f = -\frac{f - f_0}{\tau(\omega, i)} \quad (3.1)$$

where f is the phonon distribution function, f_0 is the equilibrium Bose–Einstein distribution at the local temperature, and $\mathbf{v}(\omega, i)$ and $\tau(\omega, i)$ are, respectively, the phonon group velocity and the

phonon relaxation time at a certain angular frequency ω and polarization i . $\lambda = v\tau$ is the phonon mean free path. For the multiscale simulation, because it is, in general, very challenging to solve the 3D spectral-dependent BTE, especially using deterministic methods, we here deploy a recently developed variance-reduced Monte Carlo (VRMC) method⁸⁵ to solve the BTE for the 3D experimental geometry. In the VRMC method, phonon bundles are initialized in the computational domain, and then proceed following ‘advection–sampling–scattering’ procedures¹¹⁵. In the advection procedure, the phonon bundles are moved under group velocity. In the sampling procedure, the energy carried by the phonon bundles is sampled. In the scattering procedure, the frequencies of the phonon bundles are redistributed based on the spectral distribution of the specific heat. To determine the hot-spot temperature, we calculate the temperature response to a heat pulse and integrate the response from $t = 0$ to infinity. All the material’s spectral properties for the input into the BTE simulation come from ab initio calculations and experiments.

Figure 3.3b shows the hot-spot temperature as a function of the scaling heating sizes. As expected, on reducing the heating width from 100 μm to 100 nm, the hot-spot temperature increases due to the increased packing density. We also notice that the ballistic heat transfer becomes substantial for heat spots of small sizes, so the Fourier’s law result (dashed line) deviates significantly from the BTE calculation (solid line), that is, representing practical heating behaviour. When the heating width is large, the results of Fourier’s law are consistent with the BTE, but when the heating source width is smaller than 1 μm , the hot-spot temperature from the BTE is much higher than with Fourier’s law; this difference between the BTE and Fourier’s law results increases dramatically as the width of the heating source decreases. Fundamentally, ballistic transport takes place when the heated spot size is smaller than the mean free paths, and here it

occurs for a heating source width on the order of $\sim 1\ \mu\text{m}$, which is consistent with our previous study of phonon mean free paths^{3,85,97}. The result shows that, at the nanoscale, ballistic transport will substantially increase the overheating issue over classical theory prediction.

The hot-spot temperatures are compared for the GaN–BAs device and the state-of-the-art GaN–diamond device in Figure 3.3b. This clearly shows that, for the whole range of scaling lengths, BAs has improved heat dissipation performance compared with diamond. For example, with a $1\text{-}\mu\text{m}$ heating width, the hot-spot temperature for BAs is 38% lower than that of diamond (currently the best reported in the literature for high-power cooling²³). The results demonstrate that the high G value between GaN and BAs ($250\ \text{MW m}^{-2}\ \text{K}^{-1}$), together with the high thermal conductivity of BAs ($1,300\ \text{W m}^{-1}\ \text{K}^{-1}$), substantially improve heat dissipation compared to other state-of-the-art HTC materials.

Finally, we carried out device integration with HEMTs and experimentally measured the operating HEMT devices for a comparison of the performances of the BAs, diamond and SiC cooling substrates. Figure 3.4a presents an SEM image of our fabricated HEMTs device integrated on top of a BAs substrate. In Figure 3.4b, we show the hot-spot temperature rise, while operating the AlGaIn/GaN HEMTs, as a function of power density for the different cooling substrates. With the same device layout and operating conditions, the device cooling performance for BAs exceeds that for diamond and SiC, verifying the modelling predictions. For example, at a transistor power density of $\sim 15\ \text{W mm}^{-2}$, the hot-spot temperature rise is $\sim 60\ \text{K}$ for GaN–BAs, substantially lower than the temperature rise for GaN–diamond ($\sim 110\ \text{K}$) and GaN–SiC ($\sim 140\ \text{K}$) devices.

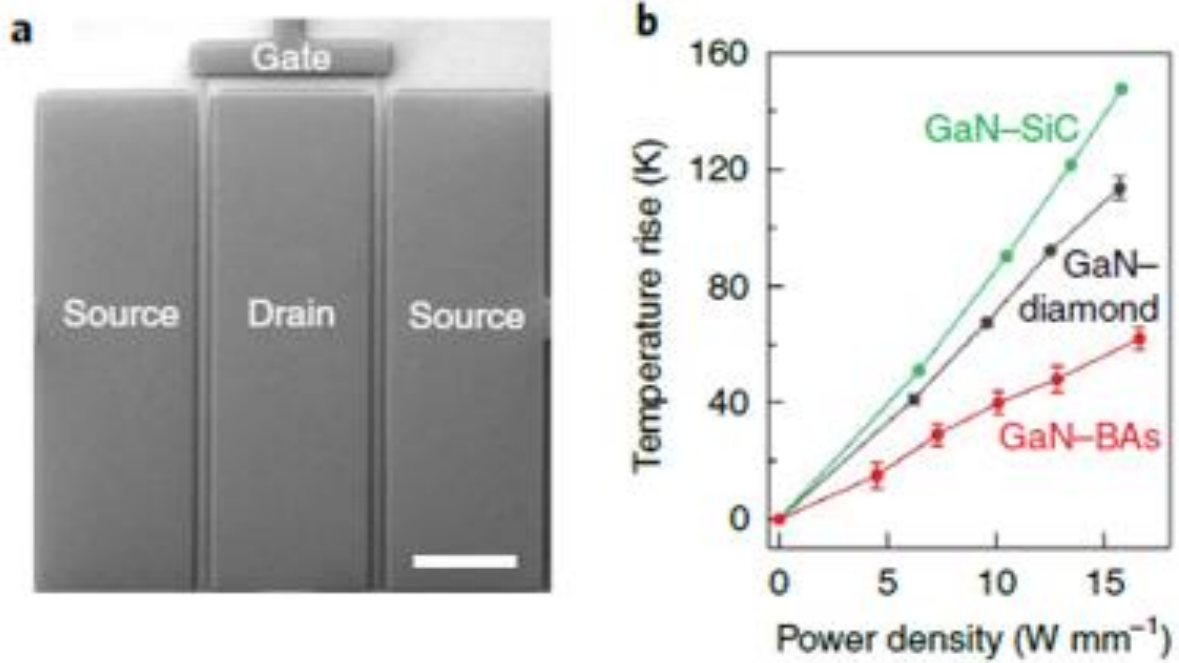


Figure 3.4: Experimental measurements of the hot-spot temperature rise in operating AlGaIn/GaN HEMTs as a function of transistor power density, with different cooling substrates (BAs, diamond and SiC). All devices shared the same geometry: two fingers, with a width of 100 μm and gate pitch of 34 μm . An SEM image of the fabricated HEMT device is shown in (a) (scale bar, 20 μm) and a plot of GaN temperature as a function of power density is shown in (b), measured using Raman spectroscopy on the drain side at a lateral distance of 0.5 μm from the T-gate edge, for transistors on a GaN-on-BAs wafer, as well as a reference GaN-on-diamond wafer and GaN-on-SiC wafer. Data for diamond and SiC substrates are adapted from ref. ¹⁰³.

3.4 Summary

We have reported the heterogeneous integration of BAs and BP as HTC cooling substrates for high-performance thermal management. Metamorphic heteroepitaxy growth was used to

fabricate BAs–GaN structures, and the thermal boundary conductance was found to offer an eightfold improvement compared with a typical diamond–GaN interface^{102–104}. The hot-spot temperatures of GaN devices integrated with different cooling substrates were examined in diffusive and ballistic regimes with length scaling from 100 μm to 100 nm. Ultrafast spectroscopy measurements and theory calculations demonstrated that interface thermal transport is substantially improved with BAs in comparison to reported state-of-the-art materials. Measurements of hot-spot temperatures of AlGaN/GaN HEMTs also showed reduced temperatures using BAs as a cooling substrate compared with diamond and SiC. Device integration of these HTC materials could improve future electronics packaging and extend the roadmap of high-power electronics.

CHAPTER 4: COMPLEMENTARY DOPING IN 2D VAN DER WAALS MATERIALS

4.1 Introduction

Previous chapters discussed about using vacuum device and using high thermal conductivity substrate for thermal management of future electronics. However, materials' thermal and electrical properties are also affected by doping. Therefore, ability to control doping is also an important aspect to be considering for efficient thermal management.

The scaling down and increasing power of modern technology components has motivated extensive studies during the last decades on the synthesis and integration of nanomaterials including nanowires^{11–15,116–120}, nanotubes^{121–130}, nanocrystals^{131–136}, and van der Waals materials^{137–147}. However, traditional doping techniques such as ion implantation routinely used in silicon industry may not be directly applicable to nanomaterials, in particular van der Waals materials due to their peculiar structures^{148–150}. Intensive efforts have been made recently in developing effective doping methods such as chemical surface modifications^{151–153}, atomic substitutions^{154–156}, gating^{157–159}, and layer stacking^{160–163} in the aim to improve the doping controllability, performance stability, and processing flexibility.

In this work, we demonstrate complementary doping of 2D materials using ionic intercalation for monolithically integrated electronics. Using black phosphorus (BP) as a model

Chapter 4 is a version of Nano Research, 2020, 13, 1369–1375. The work described in this chapter was done in collaboration with M. Ke, H. Fan, M. Li, and H. Wu. M. Ke and M. Li assisted in experiment and H. Fan and H. Wu assisted in theoretical calculation.

system, we develop both p-type and n-type transistors as well as electrical diodes as the basic electronic building elements. BP crystals were synthesized using the chemical vapor deposition method. Red phosphorus was used as the reaction source with SnI_4 and Sn as the mineralizer. The detailed synthesis procedure was reported in our recent publications^{164,165}. BP has a puckered orthorhombic crystal structure of P atoms¹⁶⁶ (Figure 4.1a). Inside a 2D layer, each P atom forms covalent bonds from the 3p orbitals: a longer bond connects the P atoms in the top and bottom planes, and a shorter bond connects the nearest P atoms of the same plane. The interlayer interaction is based on van der Waals bonding. So, the BP has three characteristic directions defined as the armchair (AC), zigzag (ZZ), and cross-plane (CP), which leads to their anisotropic properties¹⁶⁷ such as thermal conductivity^{165,168}, and interface boundary resistance¹⁶⁴. The crystal orientation is identified using angle-resolved Raman spectroscopy (Figure 4.1b): Three of the six Raman vibrational modes are detected with laser incident along the cross-plane direction following the symmetric selection rule¹⁶⁹. The three distinctive peaks appearing at 363, 440, and 467 cm^{-1} represent the vibration modes A_g^1 , B_{2g} , and A_g^2 , respectively. Note that the intensity of the Raman peaks evolves with respect to the alignment of the Raman polarization with the crystal orientation^{164,170}. For example, the maximum intensity of the A_g^2 peak corresponds to the alignment along the AC-direction (i.e. denoted as 0° in Figure 4.1b). The B_{2g} peak is maximized when the polarization is aligned precisely 45° between the AC- and ZZ-direction. Therefore, the Raman spectra data identifies the crystal orientations for the following anisotropic electrical measurements. We also note that Raman measurements taken at various locations on the samples show consistent results, indicating the uniform crystalline quality of the sample.

4.2 Local Doping Demonstration

To control the doping concentration through intercalation, we design a lithium ion battery device that allows electrochemical intercalation of Li into BP (Figure 4.1a). Thin film BP crystals with clean and smooth surfaces are formed using mechanical exfoliation to serve as the cathode of the electrochemical system. Doping of the BP sample through ionic intercalation is carefully controlled by applying a localized potential using a metal probe tip. The battery composes of a Li pellet metal (MTI Corp.) as the reference electrode and 1 M LiPF₆ salt in 1:1 w/w EC/DEC (Sigma Aldrich) as the electrolyte. More details regarding device fabrication and the in-situ electrochemical setup can be found in our recent publication¹⁶⁵. A typical galvanostatic discharge of the BP battery discharge potential versus lithium concentration (represented by x in Li _{x} P) is shown in Figure 4.1c. Starting from the pristine BP with $x=0$, discharging drives more lithium intercalation into Li _{x} P electrode and ends at the fully discharged state with $x=3$. Note that there are three main structural phases for Li _{x} P^{171,172}. For low ion concentration ($0 \leq x \leq 0.3$), physical intercalation occurs and the delithiation is highly reversible. Further discharge will induce irreversible P-P bond breaking and alloying effects¹⁷³, corresponding to a potential drop and then a wide plateau in the voltage window ($0.3 < x < 2.6$). Further discharging beyond induces phase change; at this point, the electrode becomes a mixture of Li₂P and Li₃P.

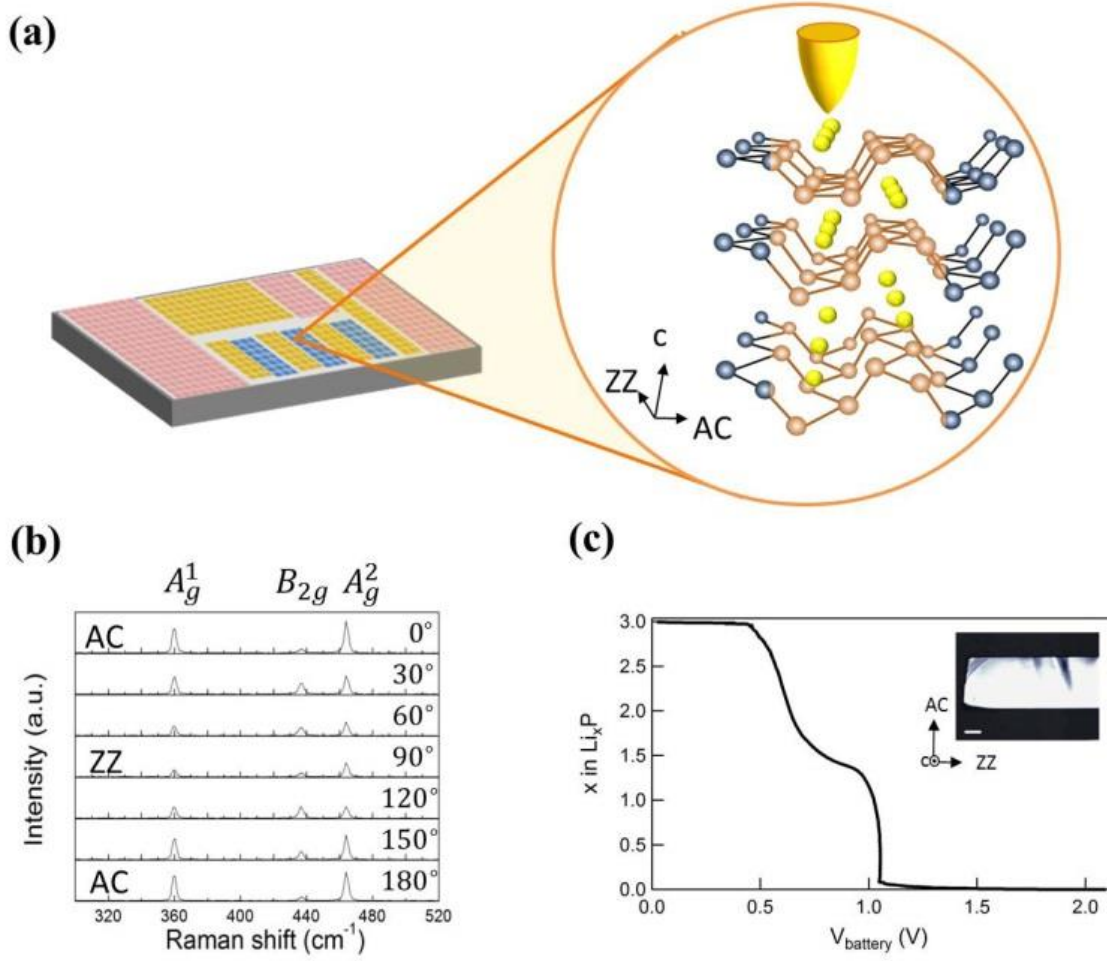


Figure 4.1: Controlled ionic intercalation to achieve complementary doping of van der Waals materials. (a) Schematic illustrating the electrochemical control for local ionic intercalations in black phosphorus (BP). The AC-, ZZ-, and c-axis denote the armchair, zigzag, and cross-plane directions respectively. (b) Angle resolved Raman spectroscopy of BP. The intensity of the three visible vibration modes are measured and used to determine the principle directions of BP. (c) Galvanostatic discharge curve for the lithium-BP devices. Inset shows the optical image of a rectangular thin film black phosphorus sample. Scale bar is 100 μm.

Next, we develop electrical diode device based on the demonstrated complementary doping. Spatially controlled doping is achieved using ebeam lithography defined patterning^{14,174}.

For example, a diode junction is formed at the interface between pristine BP and $\text{Li}_{0.7}\text{P}$ (Figure 4.2a). Under the optical image, there is a distinctive contrast indicating a clear interface: $\text{Li}_{0.7}\text{P}$ shows a dark brown in color, which has been attributed to intercalation induced phase transition and has been observed in other systems such as lithiated MoS_2 ¹⁷⁵. The difference in the Fermi levels across this heterogeneous interface forms a potential barrier (Φ) and is expected to introduce non-linear electrical transport¹⁷⁶. Our experimental measurements of such diode devices from pristine BP to $\text{Li}_{0.3}\text{P}$ (Figure 4.2b) verify such expectation: The $I_{\text{ds}}\text{-}V_{\text{ds}}$ curves evolve from linear to nonlinear and show an increased rectification effect for higher lithium concentrations. When a positive bias is applied to the diode, the Fermi energy (for holes) of the Li_3P is lowered with respect to the Fermi energy in the BP which results in a smaller potential drop across the junction. The balance between diffusion and drift is disturbed and more holes will diffuse towards the Li_3P than the number drifting into the BP. This leads to a positive current through the junction at a voltage comparable to the potential height. When a negative voltage is applied, the Fermi energy of the Li_3P is raised and now the potential across the BP now increases and further restricts the holes to the Li_3P , so that the flow of holes is limited by that barrier. This Li_3P -BP junction with positive barrier height has therefore a pronounced rectifying behavior. A large current exists under forward bias, while almost no current exists under reverse bias. In addition, the measurement shows a gradual increase in the threshold voltage of V_{ds} from around 1V to $\sim 2\text{V}$ with increased doping concentrations corresponding to increased barrier height. We further measure the temperature dependent transport of the diode from 300 to 79 K (Figure 4.2c). The diode current reduces with lowering temperature due to the suppressed thermal energy of charge carriers. The barrier potential extracted from transport measurement is $\sim 0.1\text{ V}$ for Li_3P and note that this barrier potential

remains consistent throughout the whole temperature range, indicating high stability of the intercalation doping.

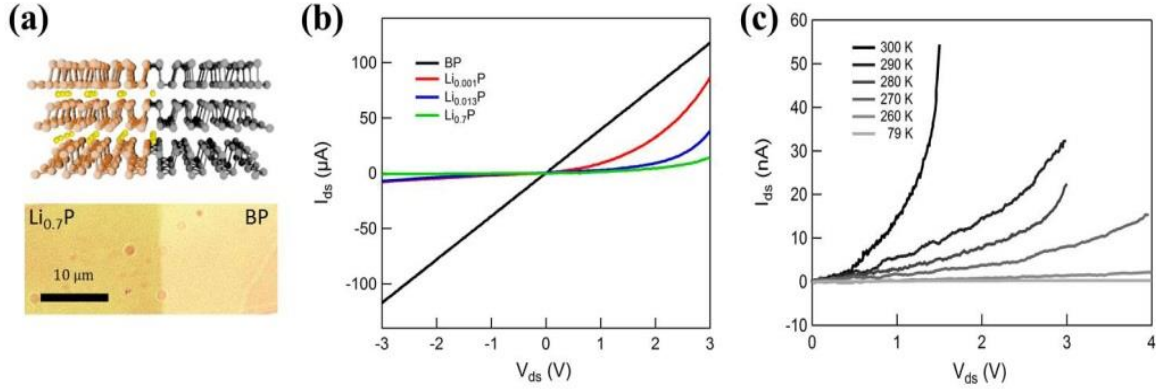


Figure 4.2: Diode device and transport characterization. (a) Schematic of form diode interface through ionic intercalation and optical image of a BP-Li_{0.7}P device, with optical contrast illustrating a clear interface. (b) I_{ds} - V_{ds} data measured of BP-Li_xP devices with different ionic concentrations. (c) Temperature dependent I_{ds} - V_{ds} data measured of a fully intercalated BP diode device.

4.3 n-type and p-type doping and FETs

As a further step, we develop both p-type and n-type field-effect transistors (FETs) based on complementary intercalation doping. For p-type devices, lithium intercalated BP is used as the semiconductor channel. The devices are fabricated using HfO₂ high- κ gate dielectrics through atomic layer deposition and metal top gate electrodes. More details regarding the fabrication have been reported previously^{13,177,178}. Typical output and transfer characteristics recorded from the pristine and intercalation devices are shown in Figure 4.3. The I_{ds} - V_{ds} curves of BP and Li_xP devices show that the drain current I_{ds} increases linearly with V_{ds} indicating ohmic source and drain contacts; the I_{ds} - V_g curves also show that I_{ds} increases as the gate voltage V_g decreases from 0 to -

1V representing a p-type enhancement-mode FET. In comparison with BP transistors (Figure 4.3b), the turn on threshold voltage (of V_g) for lithium-intercalated BP transistors (Figure 4.3d) shifts slightly towards negative voltage, consistent with hole accumulation resulted from p-type doping by lithium intercalation.

To achieve n-type FETs, we create n-type doping by using zero-valent Cu for intercalation. We use tetrakis (acetonitrile) copper (I) hexafluorophosphate precursor in mix with acetone (1 mg: 5 mL) and BP samples at 45 °C for 40 minutes to enable sufficient intercalation ¹⁷⁹. The samples are then washed with acetone and dried for transistor fabrication. The I_{ds} - V_{ds} and I_{ds} - V_g curves are measured for the Cu intercalated device (Figure 4.3e and 4.3f). The I_{ds} - V_{ds} shows linear curve indicating ohmic contact; the I_{ds} - V_g curves show that I_{ds} increases as the gate voltage V_g increases from -2V to positive voltage, representing an n-type depletion-mode FET. Note that in comparison with p-type devices, the Cu-intercalated device has a higher electrical resistance, possibly due to lower electron carrier density when converted from p- to n-type doping.

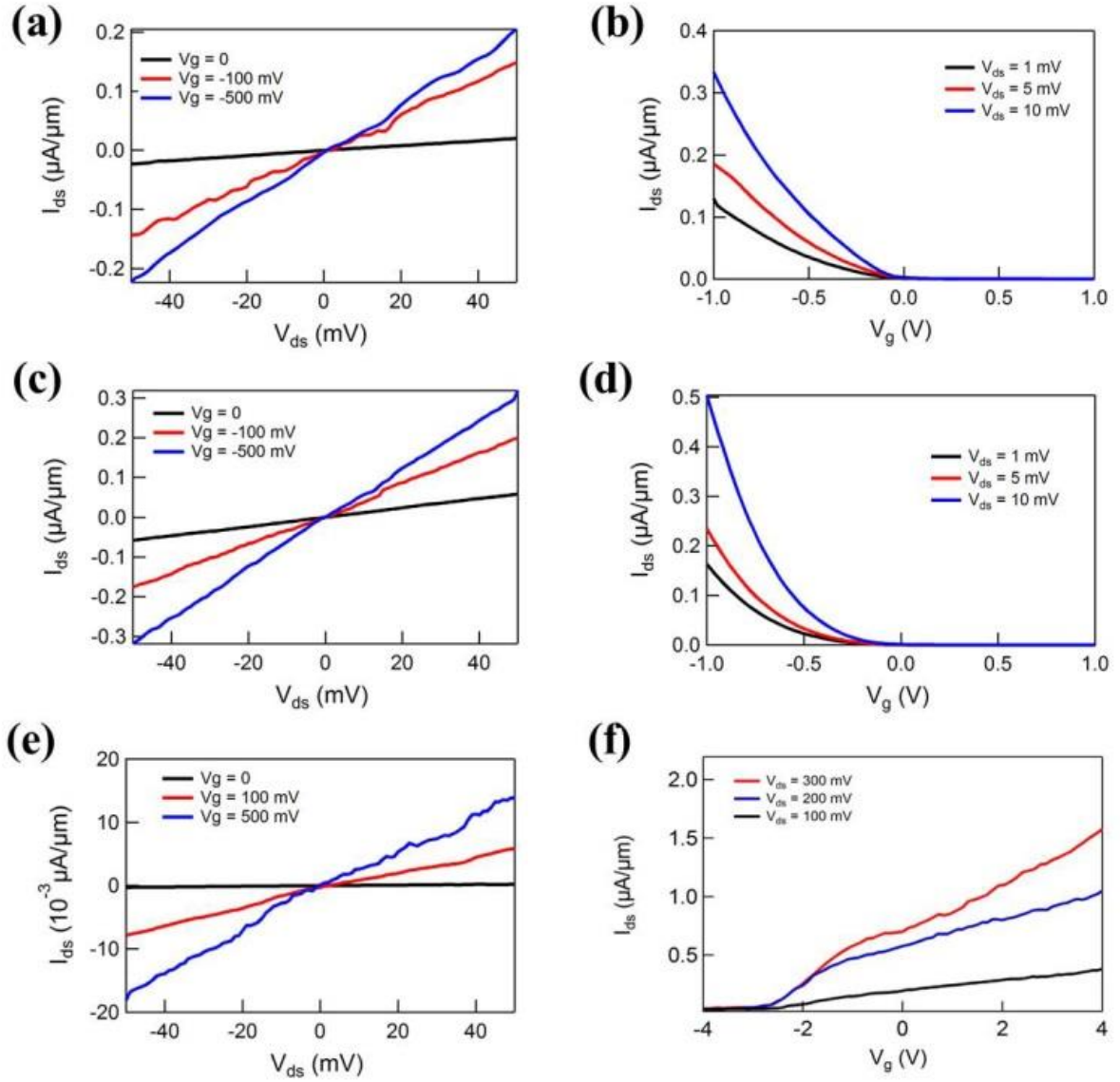


Figure 4.3: Complementary Field-effect transistors. (a,c,e) I_{ds} - V_{ds} data for devices based on BP, Li_{0.2}P, and CuP, respectively. (b,d,f) I_{ds} - V_g data for devices based on BP, Li_{0.2}P, and CuP, respectively. The former two devices represent p-type enhancement-mode FET while the latter device represents n-type depletion-mode FET.

It is interesting to note that an increase in mobility after intercalation is observed. In general, a reduction in carrier mobility is expected for common semiconductors due to stronger

impurity scattering. Here, the lithium intercalated BP samples retain p-type characteristics for different concentrations, but the hole mobility is measured to be $\sim 380 \text{ cm}^2/\text{V}\cdot\text{s}$ for pristine BP and increases to $\sim 820 \text{ cm}^2/\text{V}\cdot\text{s}$ for $\text{Li}_{0.3}\text{P}$. To better understand this phenomenon, we perform *ab initio* calculation of the band structure, density of states, and mobility for intercalated BP. The electronic band structures are calculated using density functional theory (Figure 4.4a)^{180,181} and shows a direct gap of 0.18 eV at Z point for bulk BP. Both the valence bands and conduction bands are mainly contributed by the p and s orbitals of P atoms. When Li ion is intercalated into BP, the Fermi level is shifted to the bottom of the conduction band, resulting in a p-type doping trend. The calculated density of states (DOS) shows that Li^+ does not significantly change the overall DOS since the main contributions to the total DOS is located in the deep valance band. For Cu intercalation, the fermi level shifts to the conduction band resulting in n-type doing. The Cu 3d states are hybridized with P 3p states at the top of the valence band. A small proportion of Cu 3d electrons will couple with the conduction bands. These hybridized states around the Fermi level are partly filled. To study the effects of intercalation on the charge mobility, we constructed *ab initio* electronic transport model with explicit solution to the linearized Boltzmann transport equation^{182,183}. The mobility is obtained from¹⁸⁴:

$$\mu = \frac{1}{3} \frac{\int v(k) \left(\frac{k}{\pi}\right)^2 \left(\frac{g}{E}\right) dk}{\int \left(\frac{k}{\pi}\right)^2 f dk} \quad (4.1)$$

Here, E is electric field, and $v(k)$ is the electron group velocity. f and g are electron distribution and perturbation to the electron distribution respectively, which can be solved explicitly from Boltzmann transport equation with relaxation time approximation considering several scattering mechanisms,

$$\nu_{el}(k) = \nu_{ii}(k) + \nu_{pe}(k) + \nu_{de}(k) + \nu_{dis}(k) \quad (4.2)$$

where ν_{el} , ν_{ii} , ν_{pe} , ν_{de} , and ν_{dis} stand for the elastic, ionized impurity, piezoelectric, deformation potential, and dislocation scattering rates, respectively. The presence of electrical neutral impurity (such as oxygen and water) can lead to defect scattering in addition to natural p-type dopants (such as Sn during growth) ¹⁸⁵. When the neutral impurity has a concentration higher than 10^{17} cm^{-3} , the calculation results of Figure 4.4b show that impurity scattering will significantly reduce the mobility of BP. For example, the hole mobility decreases from 816 cm^2/Vs to 336 cm^2/Vs when the impurity concentration reaches 10^{18} cm^{-3} . Although ionization leads to more impurity during lithium intercalation, the ionized impurity scattering can be relatively weaker in comparison with neutral impurity scattering due to the large 2D interlayer spacing and unique phase structures of Li_xP . Thus, we attribute the mobility enhancement to the suppressed neutral impurity after intercalation. Note that literature shows that increased hole mobility with addition of Li^+ dopant is not an isolated case in semiconductor materials. The improvement due to p-type doping has been reported and investigated for organic semiconductor¹⁸⁶ and oxide materials ¹⁸⁷. Previous study found that the effect is related to the existence of intermediate trap sites in the host crystal ¹⁸⁸. Trap sites are localized energy states within the bandgap that came from defects in the material. Excited carriers can fall into the trap sites instead of into the conduction band, thus reducing the overall mobility. Intercalation increases the number of carriers and fills up the trap sites, effectively increasing carrier mobility and conductivity.

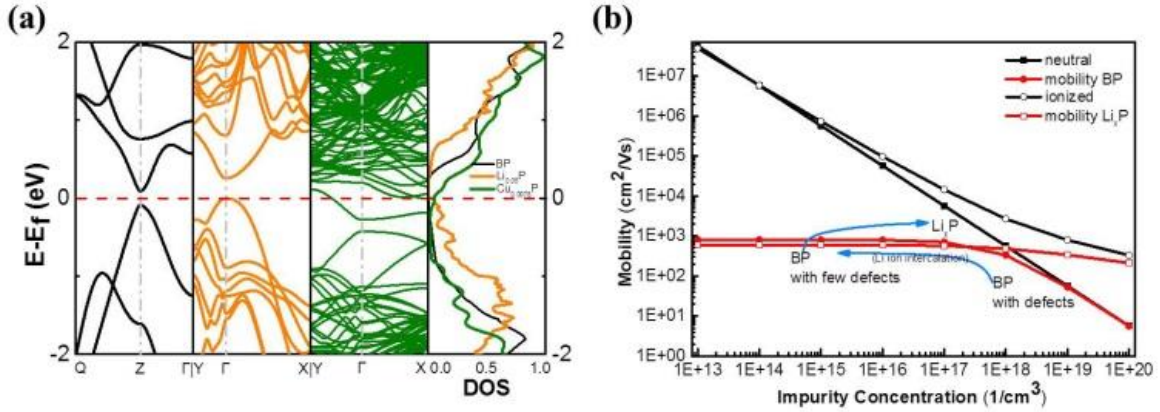


Figure 4.4: Electronic band structures and charge mobility based on DFT calculations. (a) Band structures and density of states obtained by DFT calculations. The results show no significant change to the overall DOS due to lithiation. Fermi level shift also confirms a p-type doping trend for lithiation and an n-type doping trend for Cu intercalation consistent with experimental observations. (b) Schematic illustrating effects to carrier mobility from different scattering mechanisms including neutral impurity scattering, ionized impurity scattering, for different impurity concentrations. Figure shows decreasing neutral impurity scattering and increasing ionized impurity scattering with lithiation. The contribution of neutral defect scattering decreases much faster than ionized scattering, resulting in overall mobility enhancement.

4.4 Summary

In summary, we have demonstrated complementary doping of 2D materials using ionic intercalations to achieve p-type and n-type transistors, as well as diode devices. Through the anisotropic transport study, we show that widely tunable electrical properties of black phosphorus can be achieved with high device stability and performance. In addition, mobility enhancement

through ionic doping is observed for lithium intercalated BP and verified using based *ab initio* calculations based on density functional theory. Our study provides a generic routine to control 2D building blocks with precise and local doping to achieve monolithic circuits and advanced functionalities. More generally, further extending the diversity of 2D host materials, dopants, and in combination with modern semiconductor processing, this approach could open up many new opportunities through the rational design of nanomaterials with atomic-level control.

CHAPTER 5: DYNAMIC TUNING THERMAL CONDUCTIVITY OF TIN SELENIDE BY GATE ELECTRIC FIELD

5.1 Introduction

Engineering thermal transport is crucial for a wide range of applications from microprocessors to spacecraft. The dynamic tuning of heat flow through electric gate allows for precise and on-demand modulation of heat flow and stands at the forefront of modern thermal management systems. The ability to manipulate heat flow paves the way for innovative thermal logic circuits, potentially revolutionizing beyond-CMOS applications,^{189,190} which is pivotal for effective thermal management and efficient energy utilization. Unlike the well-studied dynamical control on electrical current, such as the electrical transistor which was invented almost a century ago and is widely applied nowadays, there is few existing devices with the ability to manipulate heat flux by mean of electric gating in industrial applications. Literature have demonstrated a few processes that can achieve the tuning of thermal conductivity through mechanical switch,¹⁹¹ magnetothermal resistance effect,^{192–194} phase transitions,^{195–197} structure reconfigurations,^{198,199} electrochemical intercalations,^{200–202} and molecular junction.²⁰³ Despite these advancements, the dynamic tuning of thermal conductivity in all-solid-state devices via electrical gate voltage remains challenging, especially when it needs to be achieved without involving mechanical movement, phase transitions, or other complex operating conditions.

The work described in this chapter was done in collaboration with Z. Qin, M. Li, H. Wu, and S. Li. Z. Qin, M. Li and S. Li assisted in experiment and H. Wu assisted in theoretical calculation.

Electron-phonon interactions have been studied for nearly one century due to its essential roles in superconductivity, carrier dynamics in semiconductor, optical spectra and other properties. During the last three decades, the significant effects of electron-phonon interactions on thermal transport properties of semiconductors have been revealed theoretically and experimentally. For example, silicon showed reduction of thermal conductivity upon increased electron concentration via photoexcitation or ion doping.^{204,205} Active control of electron-phonon interactions becomes a possible approach for solid-state thermal transport modulation, however not demonstrated yet. Tin selenide (SnSe) is widely reported in literature due to its unique properties such as record high ZT thermoelectric,²⁰⁶ ultra-low thermal conductivity,²⁰⁷ unique electron band structure facilitated multiband electron transport,²⁰⁸ and low work function for high field emission.²⁰⁹ In addition, relative few studies predicted strong electron-phonon interaction within SnSe.^{210,211} In this paper, we present the development of a thermal transistor achieved by dynamically tuning the thermal conductivity of SnSe via electrical gate voltage. We achieved dynamic tuning of thermal conductivity. The tuning process involves the modulation of phonon scatterings with the localized defect electron states, achieved by activating the defect electrons when the chemical potential aligns with the defect energy level. We measure the thermal conductivity using in-situ ultrafast optical pump-probe methods. Additionally, we quantitatively analyze the localized defect electron states and their electron-phonon dynamics related to gate tuning through *ab initio* methods based on density functional theory.

5.2 Sample synthesis and device fabrication

The dynamic tuning of thermal conductivity is achieved using SnSe nanosheet (Figure 5.1a). We chose nanosheet structure due to its in-plane size and thickness are compatible with transistor fabrication and our thermal conductivity measurement. The square shaped SnSe nanosheet sample is synthesized by atmosphere pressure chemical vapor transport method inside a customized single-zone tube furnace. The precursor SnSe powders were obtained by grounding single-crystal SnSe using a mortar and pestle. More information about single crystal SnSe synthesis details can be found in our recent publication.²⁰⁷ The SnSe powder was placed into a quartz boat located upstream of the heating zone inside the quartz tube. A freshly exfoliated clean atomic-smooth mica substrate was placed onto the SnSe powders with exfoliated surface upside down. The quartz tube was pumped down to high vacuum (10^{-5} Torr) before refilling with 40 sccm of ultra-pure argon carrier gas until atmosphere pressure was achieved. This process was repeated for three times to remove the moisture and O₂ contamination before switching the argon carrier gas to 60 sccm at atmosphere pressure. The furnace was gradually heated until the center of the furnace reached 950 K. Then the SnSe powder was quickly moved to the center of the heating zone and kept at this temperature for 10 min. During this process, the SnSe powder evaporated and was transferred and redeposited. Finally, the furnace was cooled down naturally to room temperature. When the synthesis process was complete, the SnSe nanosheets were obtained on the mica substrate.

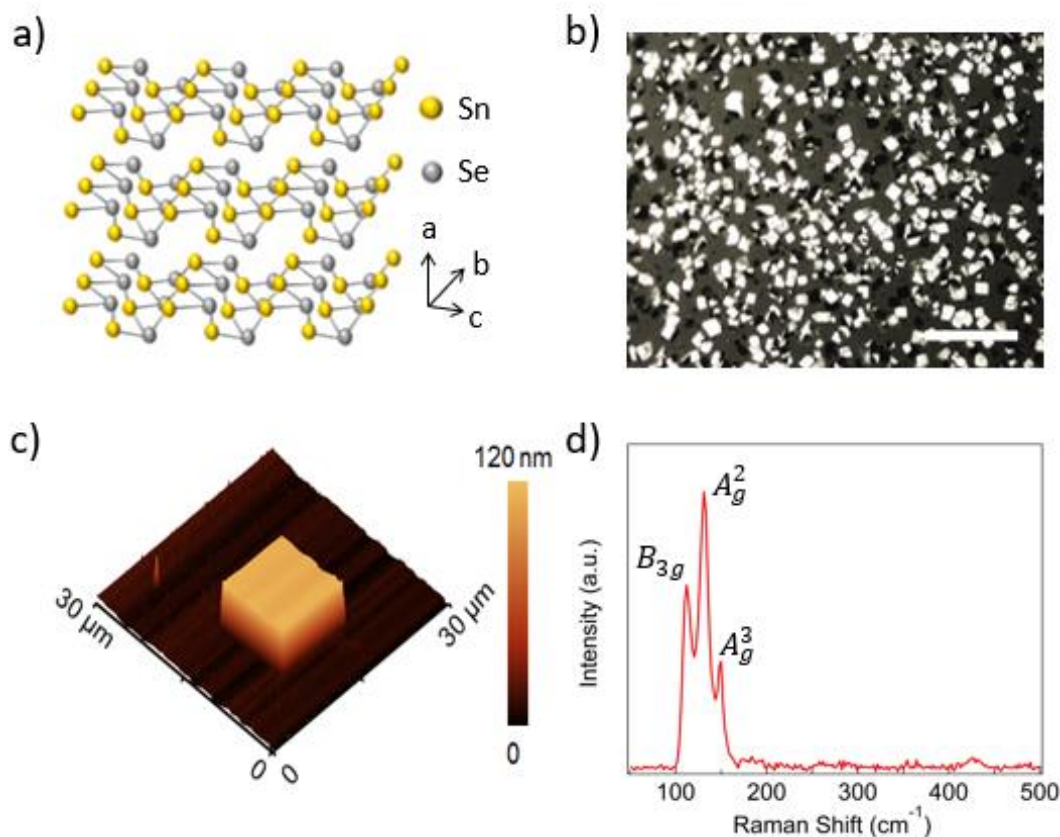


Figure 5.1: SnSe material synthesis. (a) Atomic structure of SnSe. (b) Optical image of synthesized SnSe. Scale bar is 100 μm . (c) AFM image of SnSe. (d) Raman spectroscopy measurement of SnSe.

The morphology of the as-synthesized SnSe samples was characterized by optical images and atomic force microscopy (Figure 5.1b and 5.1c). Typical optical images show that the SnSe nanosheets were randomly distributed on the mica substrate with a square shape. The samples in the optical image displayed uniform color contrast on the substrate, indicating a uniform thickness (Figure 5.1b). The thickness of the individual SnSe nanosheets was further characterized by atomic force microscopy and the height profile of a representative sample (Figure 5.1c) revealed a very flat top surface. The statistical variation of the SnSe nanosheet sample thickness were also

characterized by atomic force microscopy with a height profile between about 65-100 nm. In order to obtain details of the atomic structure, we characterized SnSe nanosheet with Raman spectroscopy. The Raman spectroscopy in Figure 5.1d shows three characteristic peaks at 110, 130, 150 cm^{-1} which corresponding to B_{3g} , A_g^2 , and A_g^3 peaks of SnSe respectively.²⁰⁷

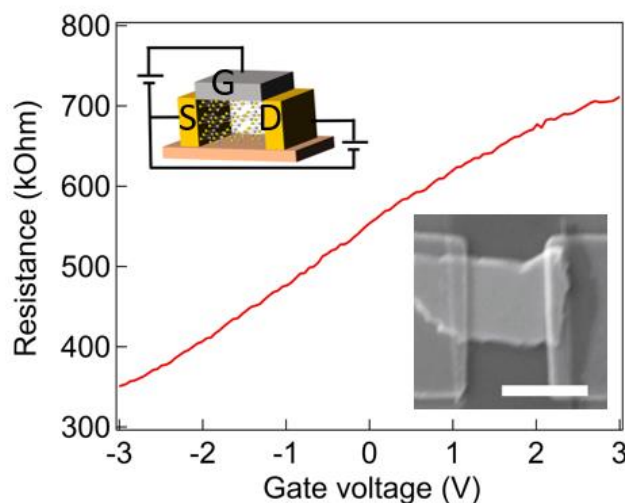


Figure 5.2: SnSe transistor. Tuning of SnSe's resistance under 50 mV source-drain bias by top gate voltage demonstrates tuning of carrier concentration. Insets are device's schematic and SEM; scale bar is 5 μm .

To make the SnSe-based thermal transistor, the SnSe nanosheet first transferred onto 300 nm SiO_2/Si wafer substrate for device fabrication. Standard electron-beam lithography is used to make source-drain and gate contact. Nickel is electron-beam evaporated to make source-drain ohmic contact. 20 nm Al_2O_3 then deposited on top of SnSe by electron-beam evaporation and ALD to make dielectric insulation for top gate. Finally, aluminum film is evaporated to make top gate. Figure 5.2 shows resistance of the SnSe transistor under gate voltage sweep. Figure 5.2 shows p-type transistor behavior in which electrical resistance increased with gate voltage due to depletion

of hole carrier. In addition, changing sample's resistance represents the modulation of carrier concentration within sample.

5.3 Thermal conductivity tuning

The dynamic tuning of thermal conductivity is controlled via electrical gate voltage and is observed in-situ using ultrafast optical pump-probe methods. To perform the in-situ thermal characterization of our fabricated SnSe-based transistors under electric field, we measured the thermal conductivity with time-domain thermoreflectance (TDTR) technique. The schematic of TDTR setup is shown in Figure 5.3a. During a typical TDTR measurement, a 800 nm femtosecond pulsed beam is supplied by a Ti:Sapphire laser and divided into two beams by a beam splitter, i.e., pump beam optically doubled by a BIBO crystal for thermal excitation and probe beam for thermal detection by relating the reflectivity of a metal transducer to temperature. By controlling the arrival time difference of two beams with a mechanical delay stage, the temperature decay of sample surface can be continuously recorded with a time resolution less than 1 ps, and fitted with a diffusive heat conduction model for thermal conductivity extraction. An electro-optical modulator and lock in amplifier was applied to improve the TDTR signal to noise ratio. The ultrafast optical thermal detection enables the non-invasive thermal conductivity measurements of nanoscale film. More details about our TDTR setup can be found elsewhere.^{85,97,106,212–214}

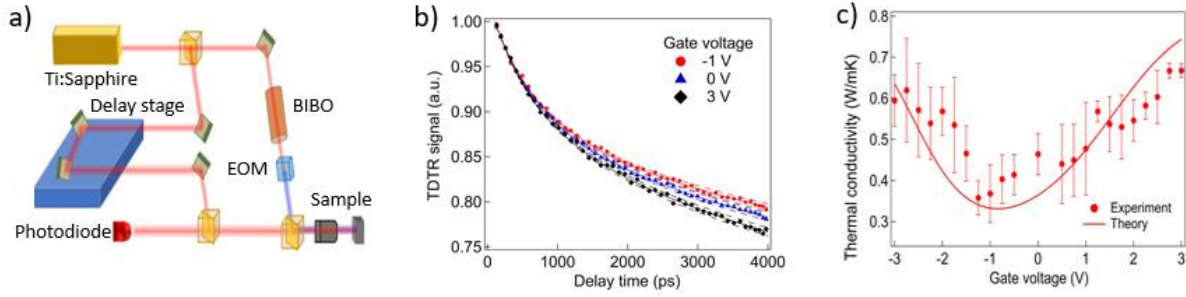


Figure 5.3: Thermal conductivity measurement. (a) Schematic of TDTR set up for thermal conductivity measurement. Blue and orange routes represent pump and probe beams respectively. (b) Representative TDTR response (close circle) versus time under different gate voltage; red, blue, and black are under -1 V, 0 V, and 3 V gate voltage respectively. Fitted data (solid lines) and calculated curves (dash lines) showed measurement accuracy within 5% error. (c) Gate voltage dependence thermal conductivity of SnSe device. Red dot is experimental data and solid line is theoretical calculation.

During thermal measurements, the SnSe transistor device source and drain are grounded and a constant voltage is applied onto the aluminum gate which generated an electric field across the SnSe sample. Simultaneously, TDTR is used to measure SnSe thermal conductivity under constant gate voltage and the aluminum gate served as transducer for the TDTR measurement. Examples of our TDTR measurement are shown in Figure 5.3b under different gate voltage. The experimentally recorded data points are well fitted by the heat conduction model (solid lines) and located between two calculated dash curves with $\pm 5\%$ thermal conductivity variation. The temperature decay rates indicate that the thermal conductivity is large at 3 V and small at -1 V. We summarized the thermal conductivity at different gate voltage in Figure 5.3c. At room temperature, we tuned SnSe thermal conductivity. Interesting enough, the thermal conductivity

trend in Figure 5.3c shows tuning behavior similar to ambipolar transistor. The ambipolar thermal conductivity trend is different from electrical trend in Figure 5.2 in which we measured monotonous p-type. To understand the measured thermal conductivity trend, we looked into the effect of defect on our device.

5.4 Device modeling and defect-dependence tuning

As-synthesized SnSe are typically p-type and have natural Sn vacancy defect which affected phonon and electron transport. Hence, it is important to characterize defect concentration within SnSe. In order to obtain details of chemical composition and defect concentration, we characterized SnSe nanosheet with XPS, EDX, and photoluminescence measurement. We characterized SnSe with XPS to measure Sn/Se ratio and to assess the Sn vacancy. Ar-ion milling is performed on the sample for one minute to remove surface impurities before XPS measurement. Figure 5.4a shows XPS results of SnSe nanosheet. The XPS peaks show Sn 3d; and Se 3d. The peaks are originated from Sn-Se bonding which are consistent with reported literature for SnSe.²⁰⁸ From the measured XPS, the peak area ratio indicates the Sn vacancy. To further verify the Sn vacancy, we use EDX to measure Sn/Se ratio for the nanosheet. We extracted the Sn/Se ratio of nanosheet from our EDX data (Figure 5.4b red data) to be 0.90 ± 0.09 . The result from EDX is consistent with XPS measurement. We further used photoluminescence measurement to characterize energy level of the defect within SnSe nanosheet. Photoluminescence data in Figure 5.4c shows three peaks which corresponding to defect level, indirect bandgap, and direct bandgap in SnSe respectively.²¹⁵ We attributed the extra peak to Sn vacancy which induced p-type doping in SnSe.

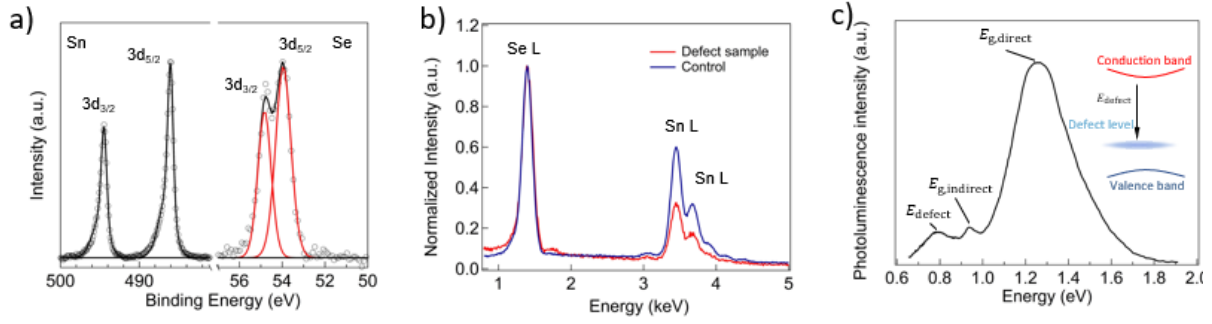


Figure 5.4: Defect characterization. (a) XPS binding energy of Sn 3d and Se 3d. (b) EDX measurement of SnSe nanosheet (red line defect sample) and single crystal SnSe (blue line control sample). Intensity is normalized with Se L peak. (c) Photoluminescence of SnSe showed direct band gap, indirect band gap, and defect state. Inset illustrated defect level within band gap of SnSe.

With information regarding to defect level of our SnSe nanosheet, we propose that the ambipolar thermal conductivity tuning arises from the alignment of the chemical potential with the defect energy level observed by photoluminescence in Figure 5.4c. This is because only the electron states near the chemical potential contribute to electron-phonon scattering, and the chemical potential is controlled by the gate voltage. When the chemical potential aligns with the defect energy level, the electrons of the defects become activated and scatter the lattice wave leading to strong phonon-electron interaction and minimum thermal conductivity. Conversely, when the chemical potential deviates from defect energy level, resulting in weaker phonon-electron scatterings and thus higher lattice thermal conductivity.

To further understand the ambipolar thermal conductivity, we calculated SnSe thermal conductivity using *ab initio* approaches based on density functional theory. The lattice thermal conductivity along α direction κ_α can be derived from kinetic theory,⁹⁸

$$\kappa_\alpha = \frac{1}{N} \sum_{qs} C_{qs} v_{\alpha,qs}^2 \tau_{qs}$$

where qs labels a certain phonon mode with wave vector $\mathbf{q}$ and branch index s . N is the number of $\mathbf{q}$ points in the mesh of the first Brillouin zone. C_{qs} , v_{qs} , and τ_{qs} are the volumetric specific heat, group velocity, and relaxation time of the mode qs , respectively. C_{qs} and v_{qs} are obtained from phonon dispersion relation, and phonon frequencies are determined by diagonalizing the dynamical matrix. Phonon relaxation times are calculated by Fermi's gold rule based on quantum perturbation theory considering phonon-phonon, phonon-isotope and phonon-electron interactions. The total phonon relaxation time is determined from different scattering mechanisms following the Matthiessen's rule,

$$\frac{1}{\tau_{qs}} = \left(\frac{1}{\tau_{qs}} \right)_{pp} + \left(\frac{1}{\tau_{qs}} \right)_{iso} + \left(\frac{1}{\tau_{qs}} \right)_{ep}$$

where $(\tau_{qs}^{-1})_{pp}$, $(\tau_{qs}^{-1})_{iso}$ and $(\tau_{qs}^{-1})_{ep}$ are phonon scattering rates from phonon-phonon, phonon-isotope and phonon-electron interactions, respectively. For phonon-phonon and phonon-isotope scatterings, the only inputs are the interatomic force constants obtained from density functional theory without using any empirical potentials or fitting parameters, and the details can be found in our previous works.^{3,216,217}

To quantitatively uncover the physics of the dynamical gate tuning on lattice thermal conductivity from the aspect of phonon coupling with localized defect electrons, here we

developed a new method to treat the phonon scatterings with localized electrons based on quantum perturbation theory. Based on Fermi's golden rule,²¹⁸

$$\left(\frac{1}{\tau_{qs}}\right)_{ep} = -\frac{2\pi}{\hbar} \sum_{mn} |g(\mathbf{qs})|^2 [f(\varepsilon_m, T) - f(\varepsilon_n, T)] \delta(\varepsilon_m - \varepsilon_n - \omega_{qs})$$

where m and n label the localized electron state. ε_n and ω_{qs} are electron and phonon energy for localized electron state n and phonon mode $\mathbf{qs}$, respectively. $f(\varepsilon, T)$ is the Fermi-Dirac distribution function at temperature T . $g(\mathbf{qs})$ is the coupling coefficient between localized electron states and phonon mode $\mathbf{qs}$, and can be modelled as^{218–220}

$$g(\mathbf{qs}) = -i \sum_j \sqrt{\frac{\hbar}{2M_j \omega_{qs}}} \mathbf{q} \cdot \mathbf{e}_{qs}^j V_0$$

where M_j is the mass of atom j . $\mathbf{e}_{qs}^j$ is the eigenvector of atom j for mode $\mathbf{qs}$. V_0 is the deformation potential defined as $V_0 = \Omega \partial \varepsilon / \partial \Omega$, which quantifies the shift of defect electron energy with respect to the relative change of the volume Ω . Assuming the deformation potential is the same for all the localized electron states, the phonon scattering rates with localized electrons is given as

$$\left(\frac{1}{\tau_{qs}}\right)_{ep} = -\frac{2\pi}{\hbar} |g(\mathbf{qs})|^2 \int \rho(\varepsilon + \omega_{qs}) \rho(\varepsilon) [f(\varepsilon + \omega_{qs}) - f(\varepsilon)] d\varepsilon$$

where $\rho(\varepsilon)$ is the density of states for localized defect electrons. The only inputs for calculating electron-phonon scattering rates is the deformation potential and the electron density of states. The deformation potential is determined from density functional theory without using any empirical

parameters. We get the deformation potential for the localized state of charged Sn vacancy ($V_{Sn}^{(2-)}$) using a supercell with 72 atoms. The electron density of states is determined by fitting the voltage and temperature dependent thermal conductivity measured by TDTR.

According to our calculation, we found that the modulation of thermal conductivity is mainly from phonon scatterings with defect electrons. Figure 5.5a shows the electronic band structure and electron density of states of SnSe calculated by density functional theory. Figure 5.5b shows the calculated phonon scattering rates at different chemical potential which we converted into gate voltage. Regardless of gate voltage, phonon-phonon scattering rates remain constant because lattice anharmonicity is independent of external electric field. Electron-phonon scattering rates are, on other hand, affected by gate voltage due to chemical potential shift. Since only the electron states near the chemical potential can scatter with phonons, the shift of chemical potential can correspondingly change the number of the electrons that participate in electron-phonon scatterings. When the chemical potential is aligns with the defect level, causing strong electron-phonon scatterings that dominates over phonon-phonon scatterings. With further increased gate voltage, the chemical potential shift up and misalign with the defect level, thus lower the electron-phonon scattering rates. The modulation of electron-phonon scattering rates with gate voltage, as shown in Figure 5.5b, results in thermal conductivity modulation. As a further step, we calculate thermal conductivity and compare with our measurement in Figure 5.3c. Our calculation matches well with our experimental data.

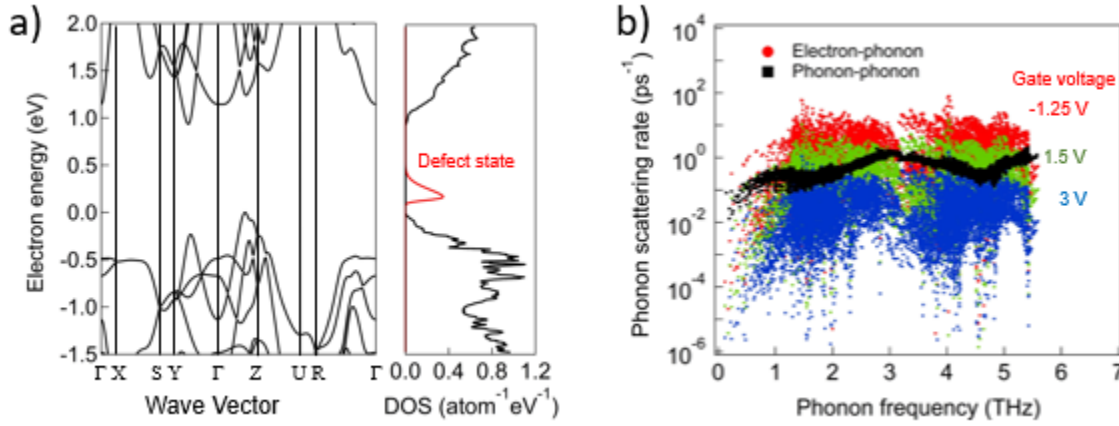


Figure 5.5: Calculation of electron-phonon interaction in SnSe. (a) Electron dispersion in SnSe (left) and density of state of SnSe and defect state (right). (b) Calculation of phonon scattering rate of phonon-phonon and electron-phonon in SnSe at different gate voltage. Red, green, and blue are electron-phonon scatter when gate voltage is at -1.25 V, 1.5 V, and 3 V respectively.

To further support our theory, we performed the measurements of temperature dependence and defect concentration dependence on thermal conductivity during gate tuning. Electron-phonon scattering rates are almost invariant with temperature, while phonon-phonon scattering rates have strong temperature dependence. As shown in Figure 5.6a, since phonons follow the Bose-Einstein distribution, the occupation number of each phonon mode has significantly decreased with lower temperature, which makes the phonon-phonon scatterings reduced greatly at lower temperature. On the other hand, under the Fermi-Dirac distribution, the occupation number of electron states are less sensitive to temperature, which makes the electron-phonon scattering rates have weak temperature dependence. Thus, we expected that when chemical potential aligns with defect level, the thermal conductivity is less sensitive with temperature due to the dominating electron-phonon

scatterings. When chemical potential misaligns with defect level, the thermal conductivity shows strong temperature dependence due to dominating phonon-phonon scatterings.

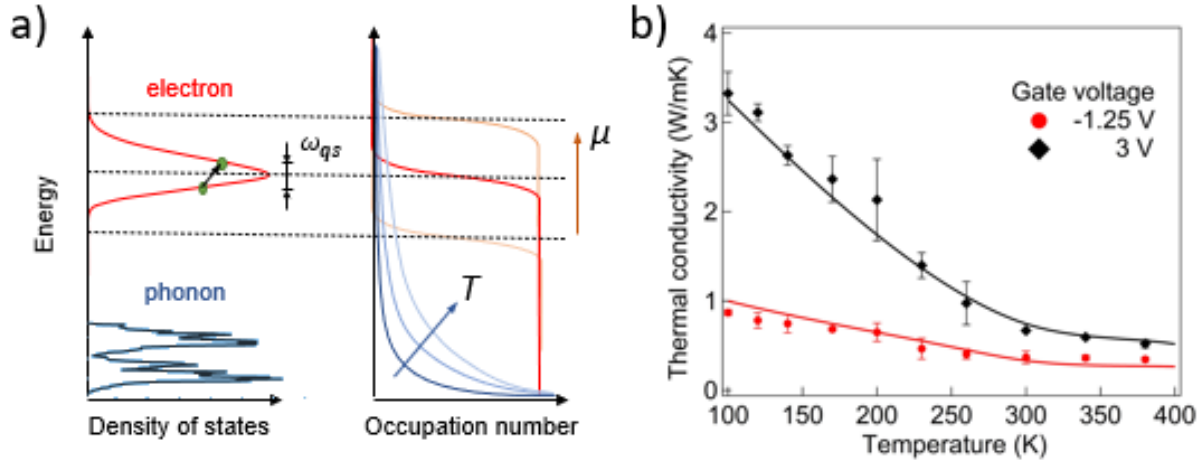


Figure 5.6: Temperature dependence thermal conductivity of SnSe. (a) Schematic of the tuning mechanism on electron-phonon and phonon-phonon interaction. (b) Temperature dependence of thermal conductivity when chemical potential aligned with defect state (red) and when mis-alignment (black). Experimental data (close circle) matched with calculation (solid line).

To validate our understandings on the tuning mechanisms based on electron-phonon scatterings, we measured the temperature-dependent thermal conductivity during gate tuning, as shown in Figure 5.6b. At a 3 V gate voltage, the thermal conductivity has large tuning. This dramatic tuning is due to the substantial suppression of electron-phonon scatterings at 3 V, and the strong temperature dependence of the dominating phonon-phonon scattering. Conversely, at -1.25 V, the thermal conductivity shows a more gradual increase. This milder increase is due to the maximization of electron-phonon scatterings when chemical potential aligns with defect energy level. Since electron-phonon scatterings have a very weak temperature dependence, the thermal conductivity becomes less sensitive to temperature changes. Our observations on the temperature

dependence of thermal conductivity are consistent with our understandings based on electron-phonon scatterings, thereby supporting our theoretical interpretation of the thermal conductivity tuning mechanisms.

5.5 Summary

In summary, we demonstrated dynamic tuning thermal conductivity of SnSe nanosheet by gate electric field. The gate electric field modulated carrier density in SnSe nanosheet which in turn scattered with phonon to tune thermal conductivity. We observed ambipolar thermal conductivity tuning. Our calculation showed that the present of defect energy level due to Sn vacancy defect is the main cause of the ambipolar thermal conductivity. In addition, we measured thermal conductivity modulation at low temperature and observed weak temperature dependence thermal conductivity due to chemical potential aligned with defect state and enhanced electron-phonon scatter. Once chemical potential no longer aligned with defect state, phonon-phonon scatter dominated and thermal conductivity began to change with temperature. Our results showed the promising application of engineering electron-phonon interaction for dynamic tuning thermal conductivity.

CHAPTER 6: ENHANCED PHONON LIFETIMES AND THERMAL CONDUCTIVITY IN DEFECT DOPED LEAD SELENIDE

6.1 Introduction

Thermoelectricity has gained much interest in recent decades due to its potential to convert heat into electricity. The key figure of merit for quantifying a thermoelectric material's energy conversion efficiency is zT , which is proportional to the material's electric conductivity and the square of its thermopower and inversely proportional to its thermal conductivity. Hence, to improve thermoelectric efficiency, many studies have been conducted to lower thermal conductivity while maintaining high electrical conductivity and thermal power, such as nanostructure engineering,²²¹ defect doping,^{222,223} and band engineering.^{206,224,225} Among thermoelectric materials, lead chalcogenides have attracted attention for applications in the mid-temperature range, between 500 K and 900 K.^{222,225–227} Lead selenide (PbSe) has been extensively studied due to its high-performance thermoelectric properties around 800 K. To improve the thermoelectric properties of PbSe, dopants are introduced into PbSe to modulate electrical conductivity and thermal conductivity. Optimization by doping metallic elements like Cu, Sb and Ag into PbSe enhanced electrical conductivity resulting in higher $zT \sim 1.6$ at 750 K,^{224,228–230} whereas dislocation doping with vacancies caused reduction of thermal conductivity and led to high $zT \sim 1.6$ at 900 K.^{222,231,232} As part of the effort to understand thermal conductivity in rocksalt II-VI materials, *ab initio* molecular dynamics calculations have related the presence of intrinsic localization modes (ILMs) in the acoustic frequency of single crystal PbSe to strong

The work described in this chapter was done in collaboration with D. Abernathy, H. Wang, M. Manley, and R. Hermann; they assisted in experiment. I acknowledge DOE SCGSR for funding this work.

anharmonicity.²³³ Because this ILM is expected to lower PbSe's thermal conductivity at high temperatures it could improve its thermoelectric efficiency. An experimental lattice dynamic study of PbSe showed the existence of optical phonon localization and ILM above 700 K²³⁴. However, a simultaneous sharpening of the longitudinal acoustic (LA) phonon mode with increasing temperature is observed and attributed to a loss of phonon-phonon scattering phase space between optical phonon and acoustic phonon, a sharpening which enhances thermal conductivity.^{234,235} The two competing effects create a plateau in PbSe's lattice thermal conductivity above 700 K at 0.7 W/m/K. It is thus interesting to investigate mechanisms that could prevent the sharpening of the LA mode to maintain lower thermal conductivity. Interestingly, lead selenide can accommodate a significant concentration of vacancies. For example, in $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$, where $\square$ denotes a vacancy and $x \geq 0.04$, the charge-neutral co-doping by two antimony and one vacancy induces a high dislocation density, and the lattice thermal conductivity continues to decrease above 700 K.²²² This suggested that high dislocation doping modifies the lattice dynamics with a different mechanism compared to undoped PbSe.

Here, we assess the impact of vacancy-induced dislocation doping on the lattice dynamics in single crystal PbSe; we used inelastic neutron scattering (INS) and thermal diffusivity measurements to study the lattice dynamics of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ at $x = 0.04$ and compared it to PbSe. We present the first full set of experimental dispersion relations. Our results revealed an unusual thermal behavior of PbSe in which defect doped single crystal $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ system shows higher phonon lifetimes and higher thermal conductivity than the more order PbSe system.

6.2 Sample synthesis and inelastic neutron scattering measurement

$\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ with $x = 0.04$ was synthesized by flux grown method using Pb, Se, and Sb materials with 99.999% metals-based purity. The $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ solid solution was prepared by melting metals inside a sealed vacuum quartz tube at 1400 K for 6 hr, followed quenching in water and annealed at 1023 K for two days.

Undoped PbSe was prepared by converting polycrystalline PbSe into large single crystal PbSe. The polycrystal PbSe was prepared by reacted Pb and Se materials with 99.999% metals-based purity in a quartz ampoule at 1100 °C. The resulting polycrystal was crushed and placed into a quartz ampoule with a tapered bottom to further refine into single crystal using gradient freeze method. During the growth process, the ampoule was supported by a quartz rod, which resulted in cold finger effect that caused a crystal to grow at top of the ampoule. Further details of PbSe and $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ can be found in Ref. ^{222,234}.

To characterize the effect of vacancy-induced dislocations on the phonon dynamic of PbSe and $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$, we measured inelastic neutron scattering (INS) of PbSe and $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ at 300 and 675 K using the the neutron time-of-flight wide angular-range chopper spectrometer ARCS at Spallation Neutron Source (SNS) at ORNL with a constant neutron incident energy of $E_i = 35 \text{ meV}$ (300 Hz chopper) mode. We used the same 8 g PbSe crystal as in Ref.²³⁴, and we used 20 g single crystal of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ with $x = 0.04$ for the measurement. The samples were aligned and placed in a furnace with vanadium sample holder. The 4D-volume data in **Q**-E space were acquired by rotating the crystal angle between the [100] axis and incident beam in 1° steps. The data were collected at each angle over 190° range at 300 K and 675 K. The

collected data were then symmetrized thrice along $[HH0] \times [H\bar{H}0]$, $[00L] \times [HH0]$, and $[00L] \times [H\bar{H}0]$ folding planes using HORACE to combine equivalent points in reciprocal space in order to improve statistic signal of a single $(\mathbf{Q}, E)$.²³⁶ A single $(\mathbf{Q}, E)$ data set is extracted with HORACE by integrated between -0.1 and 0.1 along orthogonal directions of q-axis, and integrated from -0.025 to 0.025 along q-axis at 0.4 meV energy binning in HHL projection. The processed data were then further analyzed with 1D Peak Fitting in Data Analysis and Visualization Environment (DAVE)²³⁷ and Phonon-Explorer²³⁸ to extract phonon peak energy and Γ . Phonon-Explorer fits multiple $(\mathbf{Q}, E)$ data sets simultaneously to give accurate phonon peak energy; and DAVE convolutes instrument's resolution function with a Lorentzian to extract Γ . The lattice parameter is extracted by converted the original data into $S(Q)$ with DAVE and extracted lattice parameter with FullProf.²³⁹

To further understand the temperature effect on the $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ sample, we measured inelastic scattering of the 20 g single crystal of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ with $x = 0.04$ along the Γ -K-X direction from 100 K to 725 K using HB-3 Triple-Axis Spectrometer beamline at High Flux Isotope Reactor (HFIR) of Oak Ridge National Laboratory (ORNL). We note that this is the same crystal sample we used for the ARCS beamline measurement. The spectrometer is operated with a $\lambda/2$ filter and fixed constant final energy $E_f = 14.7 \text{ meV}$ mode with horizontal collimation of 48° - 20° - 20° - 90° . The instrument used pyrolytic graphite PG(002) for the monochromator and the analyzer. The sample is mounted in a furnace with vanadium holder, and we aligned the sample to measure $[HHL]$ reflections in scattering plane. We measured the LA mode along $Q = [2+H \ 2+H \ 0]$ and TA and TO modes along $Q = [1+H \ 1+H \ 3]$ between 100 and 725 K. The phonon peak and

FWHM were extracted from HB-3 data using ResLib software package that takes into account the instrument's momentum and energy resolution (~ 1.2 meV) to fit the INS data.²⁴⁰

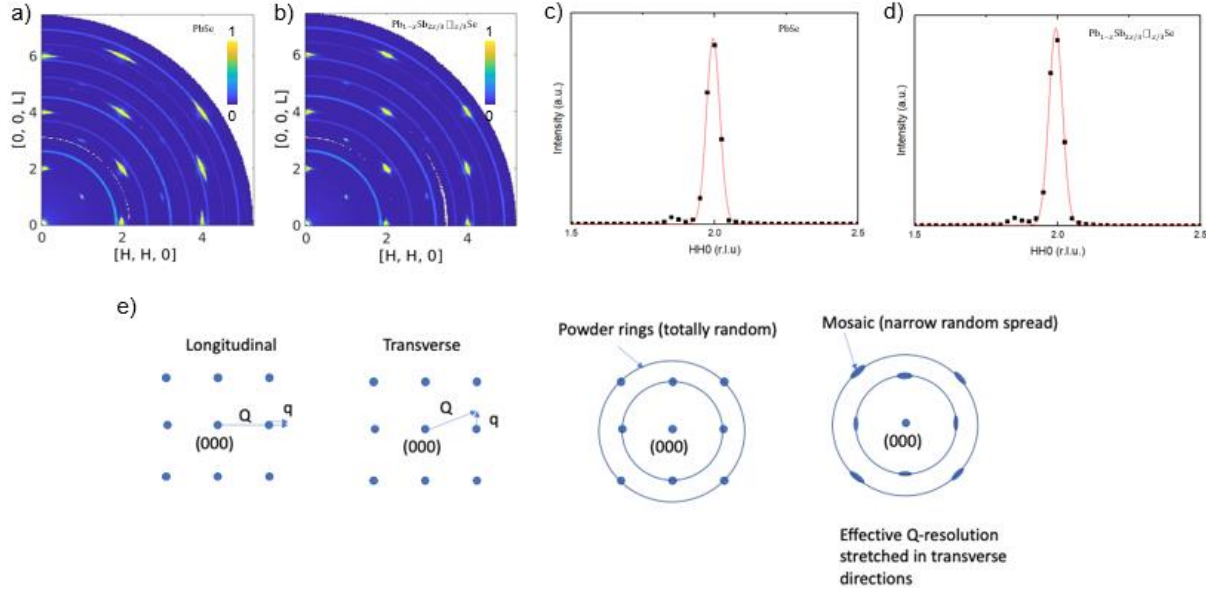


Figure 6.1: 2D Diffraction Map. Diffraction map of (a) PbSe and (b) $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ at 300 K are extracted from time-of-flight inelastic cold neutron scattering measurement with neutron scattering count integrated around elastic energy from -1 meV to 1 meV. Circular rings are from Niobium sample holder. Representative neutron scattering along radial direction at (2, 2, 0) Bragg's peak of (c) PbSe and (d) $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ at 300 K showed same FWHM with 0.0465 (4) for PbSe and 0.0474 (4) for $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$. The fitting of Bragg's peak is done using Gaussian fit. (e) Schematic of effect of mosaicity on Q-resolution of the inelastic scattering measurement.

6.3 Phonon dispersion and phonon linewidth of PbSe and $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$

The measured diffraction patterns of PbSe and $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ using the beamline ARCS at 300 K are shown in Figure 6.1a-b showed consistent Bragg's peak locations indicating that

doping does not modify the crystal's symmetry; the lattice constants are 6.1269(5) Å and 6.1166(6) Å for PbSe and $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ at 300 K, respectively, indicating a 0.17% decrease in lattice constant upon doping (Table 6.1). We note a larger mosaicity in PbSe than in $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$. This mosaicity introduces a complicating experimental factor by effectively smearing out the TA and TO modes in momentum for PbSe; however, the mosaic should not affect the measurements of the LA and LO modes. To supporting this statement, we extracted the full width half max (FWHM) of the (2, 2, 0) Bragg peak along the $[HH0]$ direction, the same direction of LA and LO modes, of the our samples. The FWHM are 0.0465 (4) for PbSe and 0.0474 (4) for $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ (Figure 6.1c and Figure 6.1d). The same FWHM along radial direction indicates mosaicity does not affect the longitudinal modes. Furthermore, the difference between a longitudinal and transverse geometry scan is that in longitudinal scan we go directly through the Bragg reflection (Figure 6.1e first picture) while for transverse geometry we move in a direction tangent to the Bragg reflection (Figure 6.1e second picture). Taken to the extreme, turning the crystal into a powder spreads the Bragg reflections over rings of constant Q magnitude (Figure 6.1e third picture). A mosaic is a small random spread on the rings. That is, the orientation of crystal is only random in a narrow range around the average angle. This will act to spread the Bragg reflection out, but only along the powder ring. This impacts the effect Q-resolution of transverse scans but not so much the longitudinal scans. The magnitude of the Q for a reflection is fixed by the d-spacing, regardless of crystal orientation.

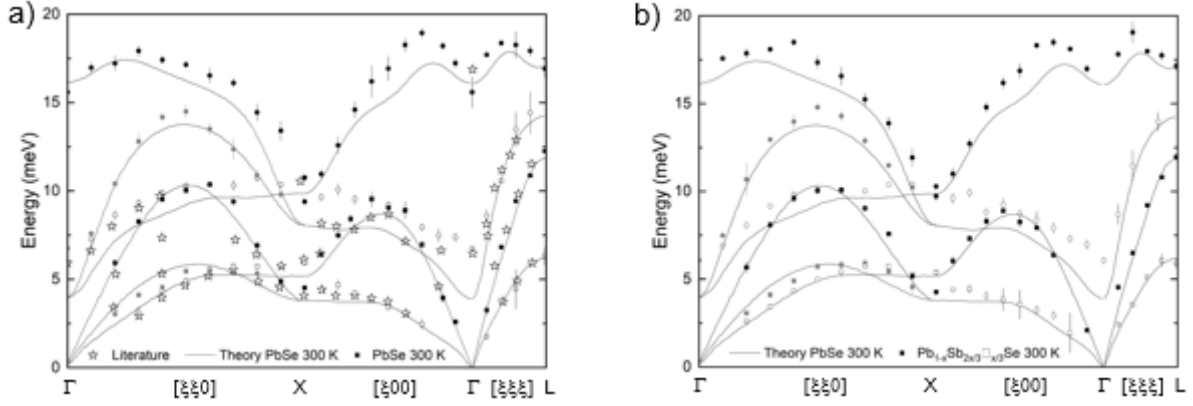


Figure 6.2: Phonon Dispersion at 300 K. Phonon dispersion of (a) PbSe and (b) $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ at 300 K extracted from time-of-flight inelastic cold neutron scattering measurement. Data points were determined by fitting Lorentzian curves to data. Error bars are fitting uncertainty. Different data symbols represent different phonon modes. Solid lines are determined from harmonic calculation for PbSe at 300 K. Literature star data points are extracted from Ref ^{235, 241}.

We extracted phonon dispersion from our ARCS measurement. Figure 6.2a and 6.2b shows phonon dispersion of PbSe and $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ at 300 K, respectively. The phonon dispersion of PbSe at 300 K showed consistent results with previous INS measurement done on PbSe.^{235,241} The harmonic approximation calculation done on PbSe at 300 K is consistent with our measurements of the acoustic modes, but underestimates the energy of the optical phonons. We attributed the difference in optical modes to anharmonicity presents in PbSe. Comparison between PbSe and $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ phonon dispersion at 300 K show little difference except at the X-point. In PbSe, there is notably larger LO-TO splitting and TA-LA splitting at the X-point. We also extracted phonon dispersions and lattice constant for PbSe and $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ at 675 K in Figure 6.3 and Table 6.1. The lattice constant of PbSe expands from 6.1269 (5) Å to 6.1760 (5) Å when

temperature increased from 300 K to 675 K, an increase of 0.80 %; for $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$, the lattice constant increases from 6.1166 (6) Å to 6.1370 (8) Å at 300 K and 675 K respectively, an increase of 0.33 %. The results show that the lattice thermal expansion of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ is lower than PbSe. Phonon dispersions in Figure 6.2 and Figure 6.3 show the energy of acoustic modes do not change significantly between 300 K and 675 K for both samples, which is consistent with previous measurement on PbSe²³⁴. However, we noticed slight hardening TO mode and softening of TO2 and LO modes of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ sample from 300 K to 675 K. For PbSe, we only observed softening of TO2 and LO modes from 300 K to 675 K. In addition, we noticed both vacancy-induced dislocation doping and increasing temperature reduce LO-TO splitting and TA-LA splitting at X-point. This suggests that vacancy-induced dislocation doping, and temperature have a similar effect on the phonons of PbSe.

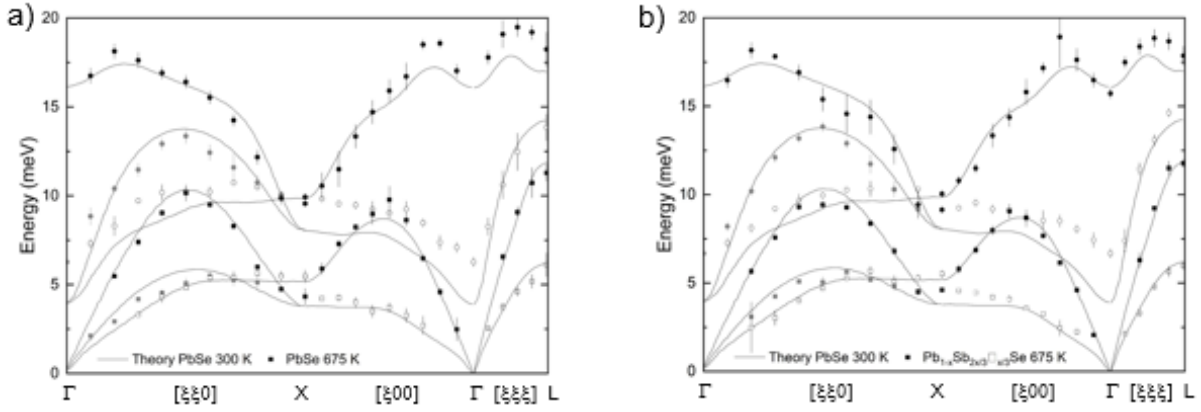


Figure 6.3: Phonon Dispersion at 675 K. Phonon dispersion of (a) PbSe and (b) $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ at 675 K extracted from time-of-flight inelastic cold neutron scattering measurement. Data points were determined by fitting Lorentzian curves to data. Error bars are fitting uncertainty. Different data symbols represent different phonon modes. Solid lines are determined from harmonic calculation for PbSe at 300 K.

Material	Temperature (K)	Lattice Constant ($\text{\AA}$)	
		300 K	675 K
PbSe		6.1269 (5)	6.1760 (5)
$\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$		6.1166 (6)	6.1370 (8)

Table 6.1: Lattice Constant of PbSe and $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$.

To further qualify the effect of vacancy-induced dislocation doping, we extracted phonon linewidth, i.e. Γ , the mode FWHM, from the ARCS data. The Γ is extracted by using the DAVE software package that takes into account the instrument's energy resolution to fit the INS data. The inelastic neutron scattering response function is modeled as a Lorentzian:

$$S(\mathbf{Q}, \omega) = [n(\omega) + 1] \frac{A_Q}{\omega_{o,Q}} \frac{\frac{1}{2}\Gamma_Q}{(\omega - \omega_{o,Q})^2 + \left(\frac{1}{2}\Gamma_Q\right)^2}$$

where A_Q , $\omega_{o,Q}$, Γ_Q , and $n(\omega)$ are fitting constant, phonon peak energy, phonon full width at half maximum, and Bose-Einstein distribution respectively.

Figure 6.4 and 6.5 summarized Γ results for all phonon modes at 300 K and 675 K. We note that Γ of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ at 300 K is generally smaller than PbSe for all phonon modes. The width, Γ , is inversely proportional to phonon lifetime, τ , according to $\tau = \hbar/\Gamma$; and thermal conductivity decreases with decreasing phonon lifetimes. In most materials, thermal conductivity decreases with defect doping due to introduction of phonon-defect scattering that reduces thermal conductivity and causes higher phonon scatter rate and increases Γ . We observed the opposite here; the defective system $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ has lower Γ than pure PbSe. The PbSe sample has larger mosaicity which artificial enlarges Γ of the transverse modes. However, the mosaicity cannot explains the abnormal Γ of longitudinal modes since longitudinal modes are unaffected by mosaicity as shown in Figure 6.1e.

To further understand the anomalous phonon properties of PbSe and $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$, we took a closer look at the inelastic scattering intensity of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ along the Γ -K-X direction from 100 K to 725 K using the beamline HB-3. Figure 6.6 summarized our HB-3 INS results. Figure 6.6a-d showed broadening of LA mode with increasing temperature which is

opposite of LA mode in PbSe²³⁴. In addition, we observed hardening and fragmentation of the TO phonon mode along with temperature in Figure 6.6e-h. The fragmentation of TO mode at high temperature has been reported in previous works for PbSe²³⁴ and NaI^{242,243}, which attributed this fragmentation of the TO mode to the formation of ILMs. We also observed the ILM in Pb_{1-x}Sb_{2x/3}□_{x/3}Se, as shown in Figure 6.6g-h, at 4~5 meV near the Γ point and only appears at high temperature, above 650 K, as in previous measurement on undoped PbSe²³⁴. Interestingly, the introduction of dislocations does not hinder formation of ILMs at high temperature.

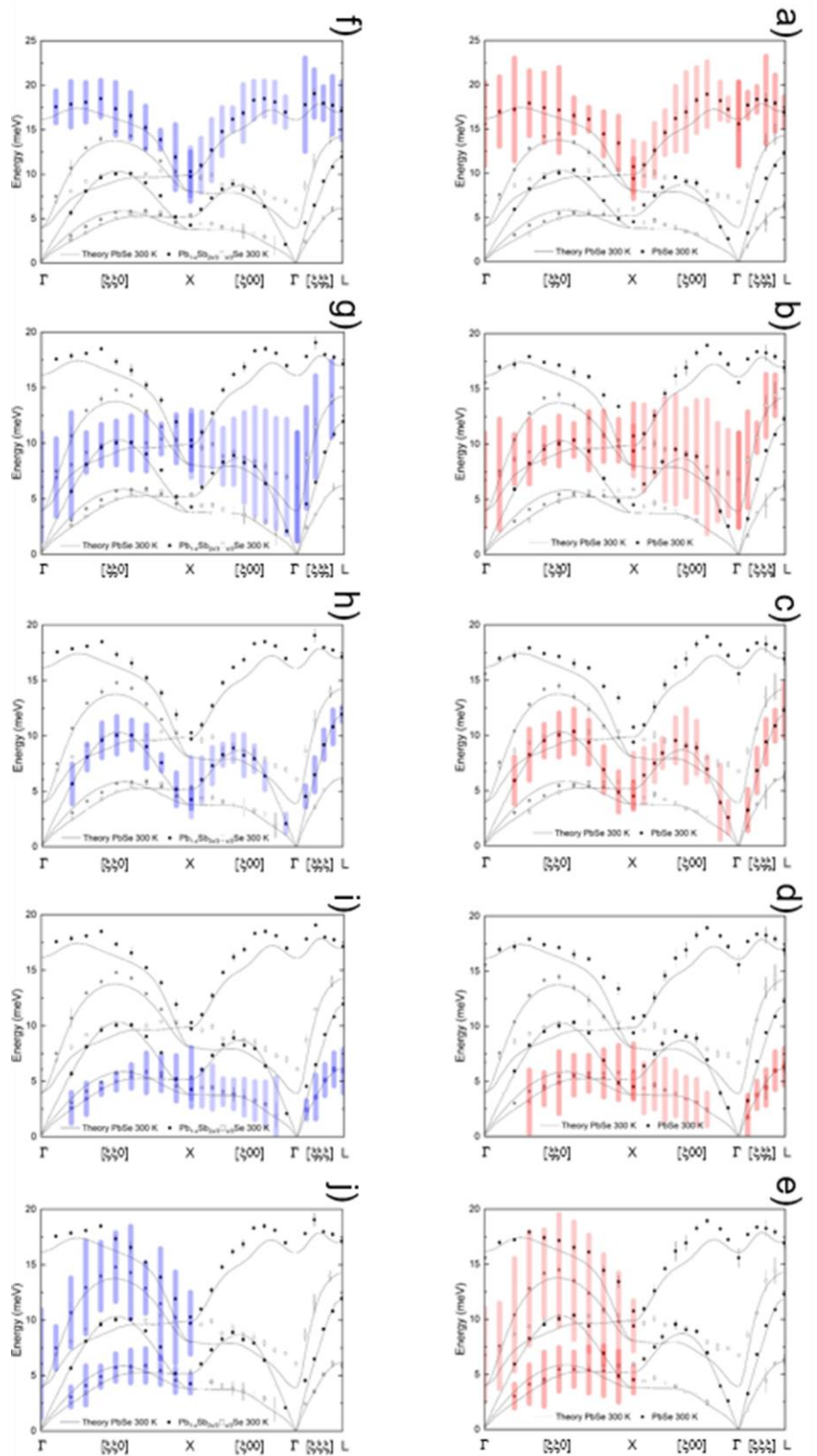


Figure 6.4: Phonon Linewidth at 300 K. Phonon linewidth, G , of (a-e) PbSe and (f-j) $\text{Pb}_{1-x}\text{Sb}_{x/3}\square_{x/3}\text{Se}$ at 300 K. The linewidth G is presented as shading red for PbSe and blue for $\text{Pb}_{1-x}\text{Sb}_{x/3}\square_{x/3}\text{Se}$ and are extracted from time-of-flight inelastic cold neutron scattering measurement. Figure (a) and (f) are LO mode, (b) and (g) are TO mode, (c) and (h) are LA mode, (d) and (i) are TA mode, and (e) and (j) are TO2 and TA2 modes.

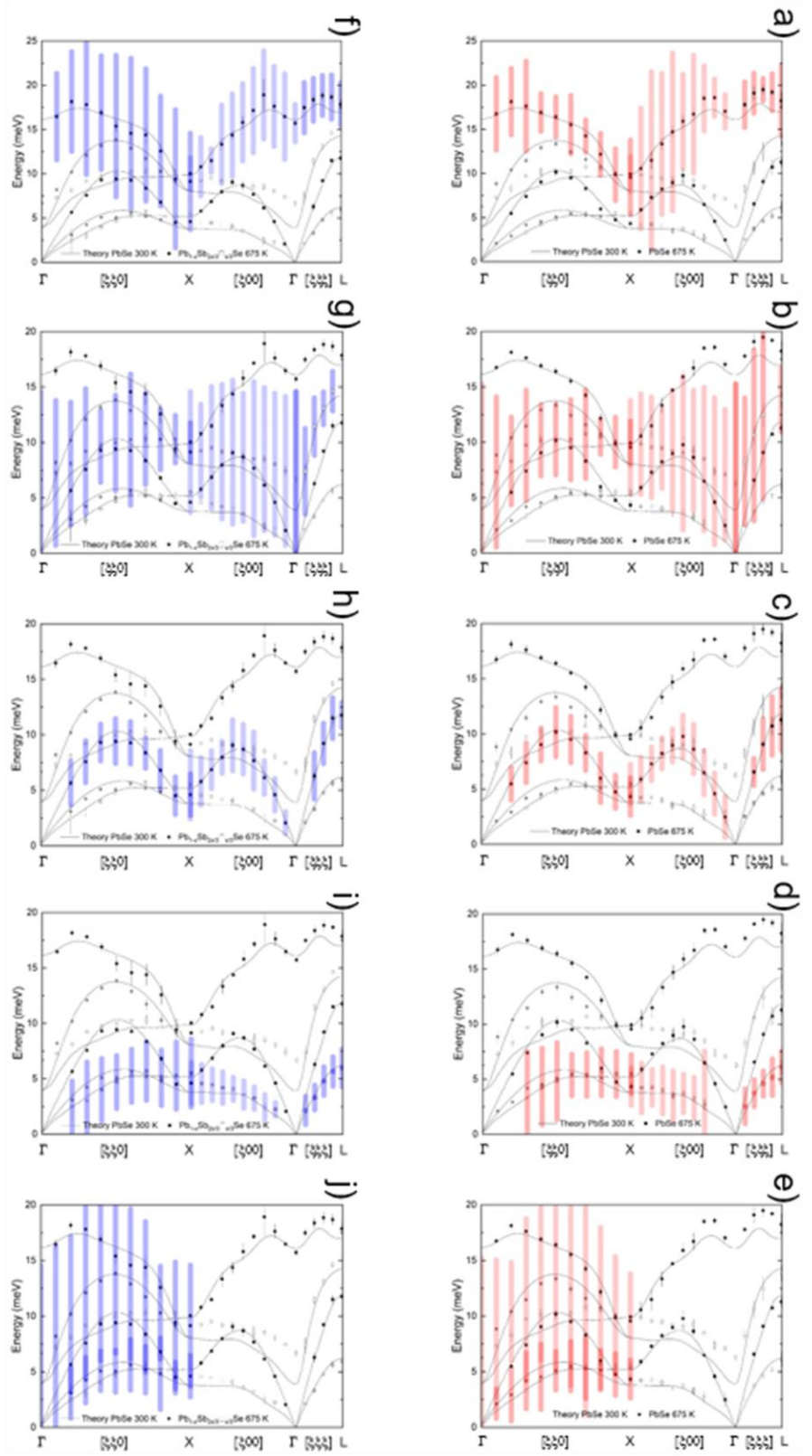


Figure 6.5: Phonon Linewidth at 675 K. Phonon linewidth, Γ , of (a-e) PbSe and (f-j) $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ at 675 K. The linewidth

Γ is presented as shading red for PbSe and blue for $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ and are extracted from time-of-flight inelastic cold neutron scattering measurement. Figure (a) and (f) are LO mode, (b) and (g) are TO mode, (c) and (h) are LA mode, (d) and (i) are TA mode, and (e) and (j) are TO2 and TA2 modes.

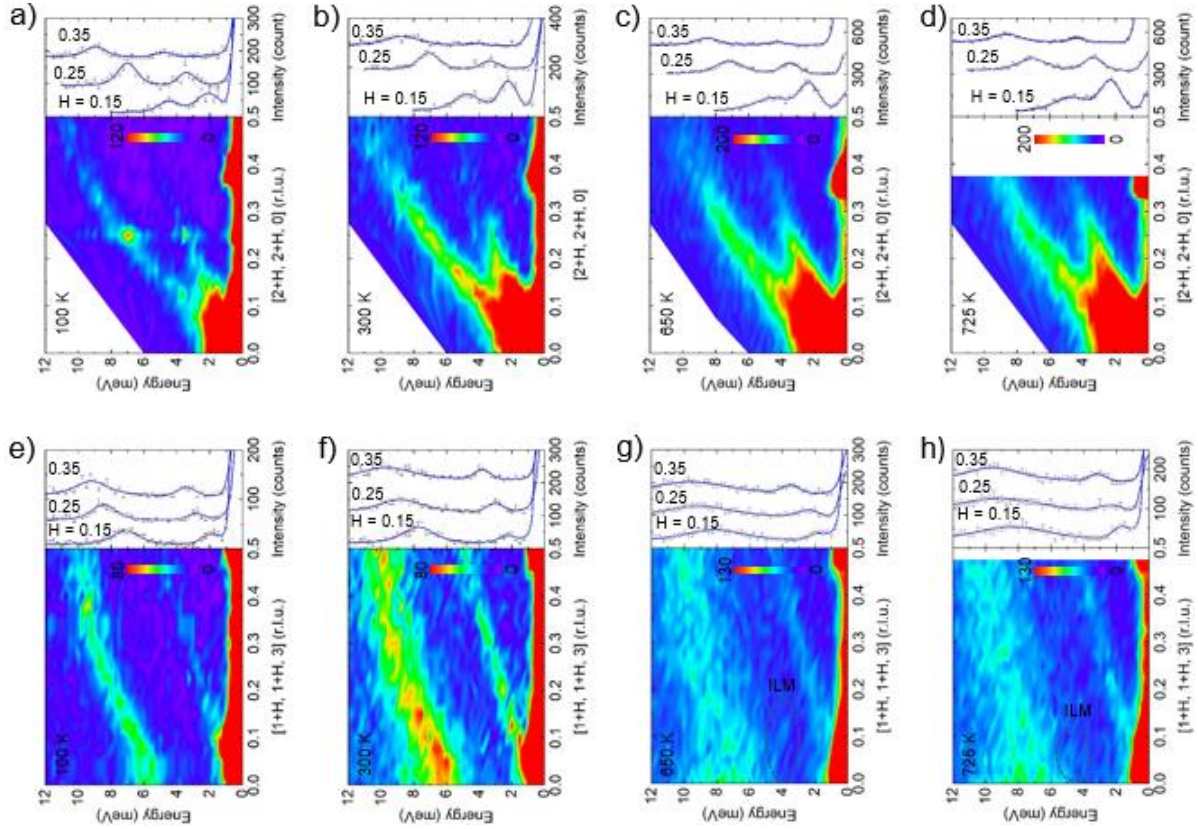


Figure 6.6: Triple-axis inelastic thermal neutron scattering measurement of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$. (a)-(d) Temperature dependence neutron scattering intensity of LA and TA2 mode along scattering wavevector $\mathbf{Q} = [2+H, 2+H, 0]$. (e)-(h) Temperature dependence neutron scattering intensity of TO and TA mode along $\mathbf{Q} = [1+H, 1+H, 3]$. Intensity color bars are in count and data sets are offset for clarity.

We extracted Γ_{LA} from HB-3 data and compared with ARCS data in Figure 6.7a. The Γ_{LA} measured from HB-3 is consistent with ARCS measurement in which the Γ_{LA} of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ lower than PbSe at 300 K. In addition, the Γ_{LA} of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ increased with temperature and plateaued around 600 K where TO fragmentation begins. On the opposite, Γ_{LA} of PbSe decreases with temperature. In most materials, thermal conductivity decreases with temperature due to

anharmonicity effect and more phonons populated with temperature caused higher phonon scatter rate and reduced phonon lifetime. This leads Γ_{LA} to increase with temperature. In PbSe, the opposite trend is observed due to reduction of scattering phase space at high temperature that prevented phonon scattering and led to reduction of Γ_{LA} .²³⁴ We observed a broadening of the LA phonon in $Pb_{1-x}Sb_{2x/3}\square_{x/3}Se$ with increasing temperature due to dislocation doping prevents the sharpening of the LA mode in comparison to undoped PbSe. In addition to the LA mode, we extracted the linewidth of TO mode at $Q = [1.25 \ 1.25 \ 3]$ (Figure 6.7b) and observed both $Pb_{1-x}Sb_{2x/3}\square_{x/3}Se$ and PbSe have comparable Γ_{TO} at 300 K and 675 K. This suggests that vacancy-induced dislocation doping mainly affects the LA branch and its width in PbSe while the Γ of the other modes still broadening with temperature according to anharmonicity effect.

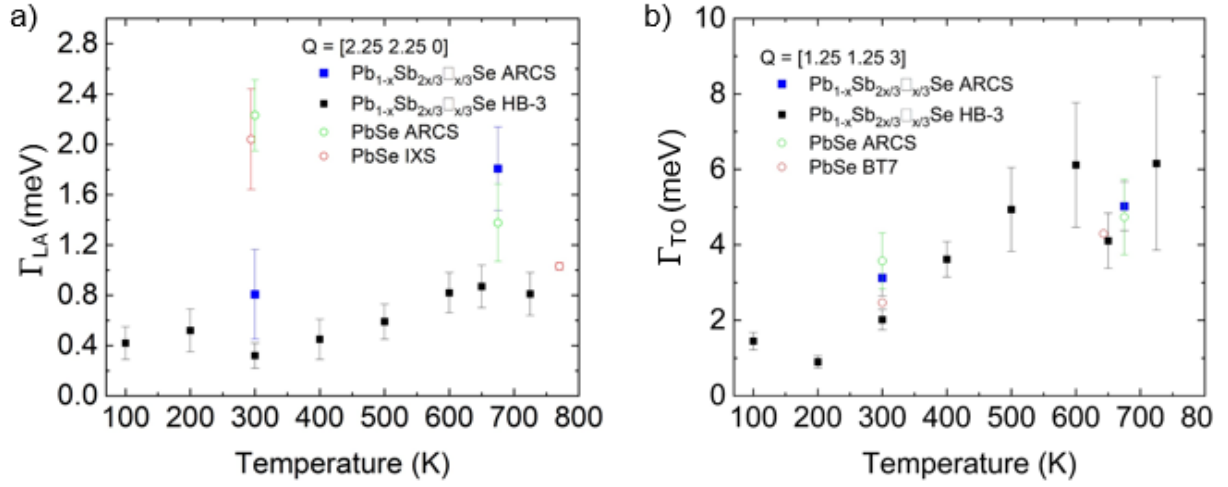


Figure 6.7: Representative Temperature Dependence Phonon Linewidth. Temperature dependence phonon linewidth Γ of (a) LA mode at $Q = [2.25, 2.25, 0]$ and (b) TO mode at $Q = [1.25, 1.25, 3]$. Black and blue square data points are from $Pb_{1-x}Sb_{2x/3}\square_{x/3}Se$ sample measured with triple-axis HB-3 and time-of-flight ARCS respectively. Green circle data points are from $PbSe$ sample measured with time-of-flight ARCS; and red data points are from $PbSe$ sample extracted from Ref ²³⁴.

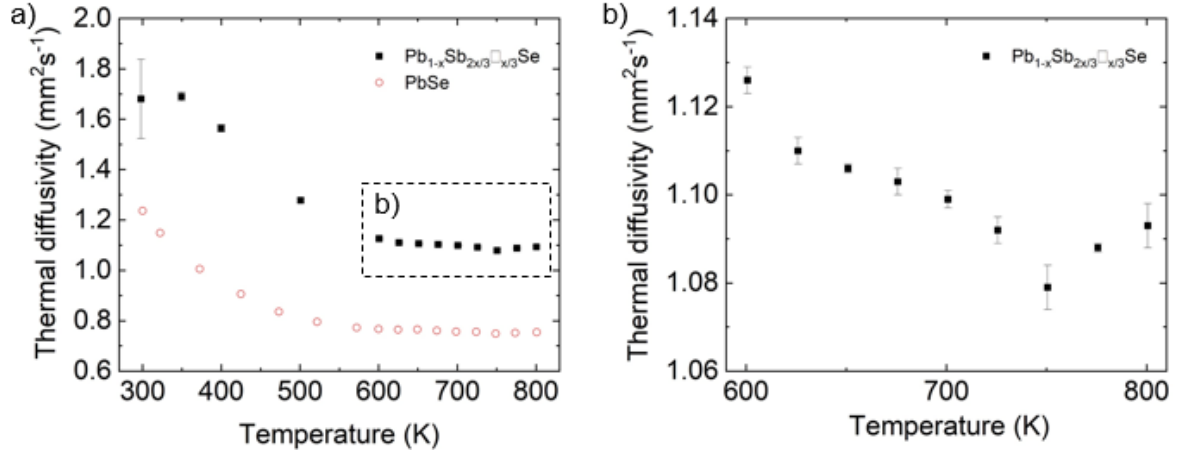


Figure 6.8: Thermal Diffusivity Measurement. Thermal diffusivity of PbSe and $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ at (a) 300 K to 800 K and (b) a close-up view of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ at 600 K to 800 K. Black data points are measured thermal diffusivity of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ and red data points are thermal diffusivity of PbSe extracted from Ref ²³⁴.

6.4 Thermal diffusivity and thermal conductivity of PbSe and $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$

To relate the effect of vacancy-induced dislocation doping and of the anomalous Γ_{LA} on thermal properties, we measured thermal diffusivity of single crystalline $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ from 300 K to 800 K. Thermal diffusivity was measured using a NETZSCH LFA457 laser flash system. It follows ASTM E1461. The system uses an Nd-YAG laser to deposit a short heat pulse (0.1–1.0 ms) to heat up the front surface of a sample and an InSb IR detected measures the back-surface temperature rise. Thermal diffusivity is calculated using Cowan’s method²⁴⁴ with pulse-width correction. Thermal diffusivity was measured from 300 to 800 K in 50 K increments under argon purge gas at 100 ml/min. Thermal diffusivity results can be used to calculate thermal conductivity using: $k = \alpha\rho C_p$ in which α is thermal diffusivity, ρ is density, and C_p is the specific heat. The

density and specific heat are assumed to be same for both PbSe and $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ and extracted from Ref.²⁴⁵. Thermal diffusivity of PbSe is extracted from Ref.²³⁴. Lattice thermal conductivity is extracted by subtract the electronic contribution: $k_l = k - k_e$ and $k_e = LT\sigma$ where L is Lorenz number and σ is electrical conductivity. Electrical conductivities are extracted from Ref.^{222,234}.

Figure 6.8a showed that the thermal diffusivity for $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ is higher than in PbSe which is consistent with the smaller Γ_{LA} . In addition, we took a closeup view of the thermal diffusivity of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ from 600 K to 800 K as shown in Figure 6.8b and saw the small kink at 750 K. Coincidentally, this small kink occurred at temperature where electrical behavior of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ changed from metallic-like to semiconductor-like.²²² To remove the electrical contribution, we extracted lattice thermal conductivity of PbSe and $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$. The lattice thermal conductivity of PbSe shows a small kink at 750 K due to the sharpen of Γ_{LA} (Figure 6.9a); however, the lattice thermal conductivity of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ showed constant plateau from 700 K to 800 K (Figure 6.9b) which is consistent with plateau Γ_{LA} and Γ_{TO} of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ measured from HB-3 in Figure 6.7.

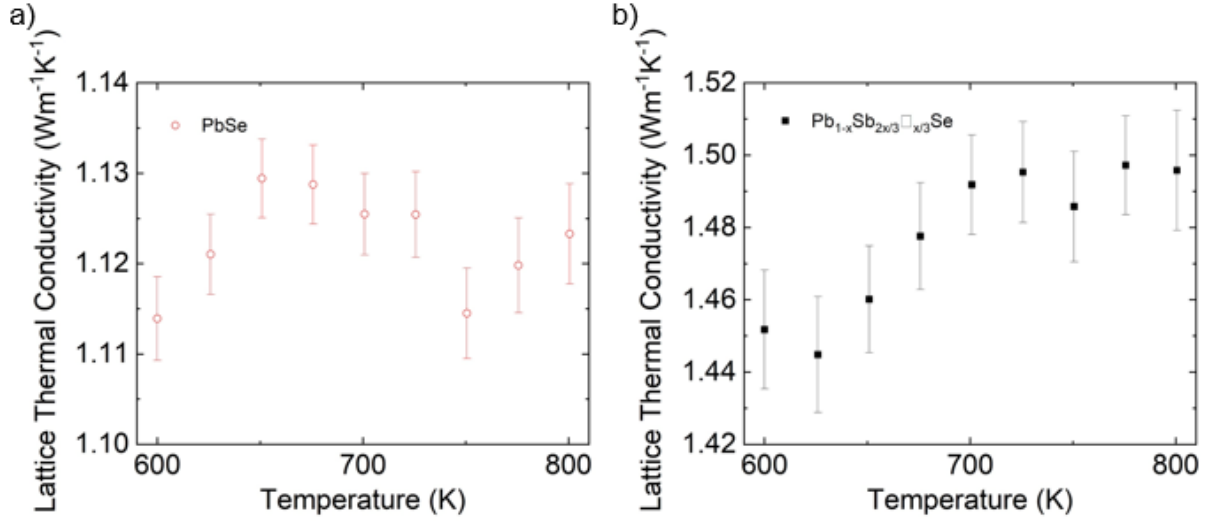


Figure 6.9: Lattice Thermal Conductivity. Lattice thermal conductivity of (a) PbSe and (b) Pb_{1-x}Sb_{2x/3}□_{x/3}Se.

6.5 Summary

We have presented the phonon dispersion and phonon linewidth of PbSe and Pb_{1-x}Sb_{2x/3}□_{x/3}Se. Our results showed anomalous thermal properties of Pb_{1-x}Sb_{2x/3}□_{x/3}Se where defective sample possess higher phonon lifetime and higher thermal diffusivity than the more order system PbSe. Our results are anomalous comparing to other materials in literature where defect doping caused reduction of phonon lifetime and thermal conductivity. We believe more theoretical calculation is needed to further explain our observation; however, theoretical calculation is beyond the topic of this chapter and we will further explore in our future work. Overall, our results provide additional insights to engineering thermal properties of lead chalcogenide materials.

CHAPTER 7 CONCLUSION

Modern electronics rely on size scaling to enhance performance. With reduction of device sizes, the power density required to dissipate increase and is expected to be as high as 1000 watts per square centimeter. This magnitude of power density leads to device degradation and diminished performance. Hence, there is an urgent need for methods and novel materials to minimize heat generation and for efficient thermal management approaches while enhance electrical performances of the future electronics. In this dissertation, I investigated effect of nanostructuring and defect doping as approaches to control electron and phonon transport. My experimental results provide additional insight on tailoring materials' electron and phonon properties and thus provide an additional avenue for achieving efficient thermal management and high electrical performance.

I nanostructured SnSe nanoflower morphology to achieve sharp nanostructure for field emission application. I demonstrated high-performance and stable field emission of single SnSe nanostructures in air with the device channel down to 100 nm. The SnSe nanoflower showed low operation voltage as low as 0.5 V and high field enhancement factor. In addition, the channel lengths-dependence of field enhancement factor showed unintuitive high field emission performance at small channel; suggesting the field emission device can further improve by reducing device's size. The results show that SnSe nanostructured is a promising material for field emission applications and underscores the promise of rational materials design at the nanoscale to develop new building blocks beyond conventional electronics.

In addition to material nanostructuring, I demonstrated device nanostructuring by demonstrating high thermal boundary conductance by Debye temperature matching in GaN-BAs integration. Considering that GaN and BAs have different lattice structure and different growth temperatures which hindered epitaxial growth of GaN on top of BAs; thus I used metamorphic heteroepitaxy approach for GaN-BAs integration. With this approach, the thermal boundary conductance across GaN and BAs interface is as high as $250 \text{ MW m}^{-2} \text{ K}^{-1}$. To further demonstrate the thermal management BAs substrate, I fabricated AlGaIn/GaN-BAs electronics device and measured device's temperature during operation. The results showed AlGaIn/GaN-BAs have lower temperature compared with diamond and SiC. Device integration of BAs could improve future electronics packaging and extend the roadmap of high-power electronics.

Aside from nanostructuring, electronics' performance can be improved through defect doping. To demonstrate this, I introduced defects into black phosphorus, SnSe, and PbSe and measured electron and phonon transport of defect-doped samples. I doped black phosphorus using ion intercalation approach to introduce lithium ion and copper ion doping. The copper doped black phosphorus converted pristine p-type black phosphorus into n-type semiconductor as shown in n-type CuP transistor device. The lithium doping increased hole concentration as demonstrated in LiP-P diode device where LiP-P interface formed an energy barrier due to difference in hole concentration at two sides; and thus the diodity of the LiP-P diode is tuned through controlling lithium doping concentration. In addition, lithium doping enhanced hole mobility due to suppression of electron-neutral defect scattering upon introduction of lithium ion. This study provides a generic routine to control 2D building blocks with precise and local doping to achieve monolithic circuits and advanced functionalities.

For the SnSe, I investigated the effect of vacancy defect on phonon transport in SnSe. In this study, I demonstrated dynamic tuning thermal conductivity of SnSe by using electrical gate voltage. The electrical gate tuned Fermi level of SnSe to align with the defect level, by doing so, the electron-phonon scattering rate in SnSe is tuned and thus modified thermal conductivity of SnSe. This is demonstrated in SnSe thermal transistor device where constant gate electric field is applied and the thermal conductivity is measured by TDTR method. With this approach, the thermal conductivity is tuned. The results showed the promising application of engineering electron-phonon interaction for dynamic tuning thermal conductivity.

Finally, I studied the effect of vacancy-induced dislocation doping in PbSe by using inelastic neutron scattering method and thermal diffusivity measurements to study the lattice dynamics of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ at $x = 0.04$ and compared it to PbSe. The results showed anomalous thermal properties of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\square_{x/3}\text{Se}$ where the doped sample showed higher phonon lifetime and higher thermal diffusivity than the more order system PbSe. The results provide additional insights to engineering thermal properties of lead chalcogenide materials.

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