Thermal characterization of nm-thick black phosphorus based on Raman spectroscopy

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Thermal characterization of nm-thick black phosphorus based on Raman spectroscopy

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The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

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ABSTRACT

As a new two-dimensional material, black phosphorus has attracted worldwide attention due to its extraordinary electronic and optoelectronic properties. Despite its importance for the performance of electronic devices, thermal properties of black phosphorus are still not well studied, which leads to incomplete understanding on phonon transport and interaction in black phosphorus. This is related to difficulties for preparing black phosphorus samples since black phosphorus is easily oxidized in air and the difficulty in characterizing this nm-thin material. In this work, black phosphorus is studied systematically with techniques developed based on Raman spectroscopy. Our study on black phosphorus involves identifying its crystalline orientation and measuring its interface thermal conductance and anisotropic in-plane thermal conductivity.

In this work, the crystalline orientation of black phosphorus is identified with a newly developed technique, optothermal Raman spectroscopy. This technique utilizes the anisotropic heating effect of a linear polarized laser for crystalline orientation identification. It can distinguish the armchair direction and zigzag direction precisely regardless of excitation wavelength and sample thickness. This in-situ and nondestructive technique is required to identify the crystalline orientation of black phosphorus samples before their interface thermal conductance and anisotropic in-plane thermal conductivity are measured. Interface thermal conductance between black phosphorus and Si is measured with micro-Raman spectroscopy. It is found there is large interface thermal conductance between black phosphorus and its adjacent Si, which suggests black phosphorus can be used as new interface material for future devices. Also, interface thermal conductance shows a strong negative correlation to temperature, while no
correlation to thickness. These results lead to the discovery of the temperature-related morphological variation of supported black phosphorus on Si. Frequency-resolved Raman spectroscopy is developed to measure the anisotropic in-plane thermal conductivity of black phosphorus. This technique is first used to measure thermal diffusivity of a c-Si cantilever, which has a reference value of thermal diffusivity. The validity of this technique is sufficiently verified since our measured thermal diffusivity is very close to its reference value. Our measurements on black phosphorus with thickness between 99.8 and 157.6 nm show the armchair thermal conductivity is $13.5\sim22\ \text{W m}^{-1}\text{K}^{-1}$, and the zigzag thermal conductivity is $39.8\sim62.7\ \text{W m}^{-1}\text{K}^{-1}$. These studies significantly advance our fundamental understanding of phonon transport and interaction in black phosphorus, which can further benefit the development of new-generation devices.
CHAPTER 1. INTRODUCTION

1.1 Black Phosphorus and its Thermal Properties

Continuous scaling down of conventional complementary metal-oxide-semiconductor (CMOS) devices is approaching a saturation point. To scale down the size and advance the performance of electronic devices furthermore, researchers are in the quest of searching new-generation materials as building blocks for constructing electronic devices. Graphene has gained overwhelming interests since its discovery by Novoselov and Geim in 2004. As the first successfully isolated two-dimensional material, graphene has demonstrated remarkable mechanical, electronic, optical and thermal properties. These exciting findings on graphene have inspired rapidly growing research efforts on other two-dimensional materials, such as transition metal dichalcogenides (TMDCs), hexagonal boron nitride (hBN) and black phosphorus (BP).

As the newest member of two-dimensional materials, BP owns many extraordinary properties, such as high carrier mobility (~1000 cm² V⁻¹ S⁻¹ in field-effect transistors) and thickness-dependent direct bandgap, which varies from 0.3 eV (bulk) to 1.4 eV (monolayer). Most intriguingly, with a puckered honeycomb structure, BP exhibits unique anisotropy in its optical, electrical, thermal and mechanical properties, which is commonly characterized by two high-symmetry lattice directions, the armchair direction and the zigzag direction. These properties make BP become an ideal platform for designing and fabricating novel devices. So far, BP has been successfully integrated into various electronic and optoelectronic devices. For nano/microscale BP devices, their performance is not only directly determined by BP’s
electrical properties, but also relevant to BP’s thermal properties, especially interface thermal conductance and in-plane anisotropic thermal conductivity. Therefore, the successful application of BP-based devices requires a fundamental understanding on the thermal transport in BP. However, experimental studies on BP’s thermal properties are challenging since BP is easily oxidized in air and it has relatively small sample size.

Despite these difficulties, Luo et al. pioneered measurements of the anisotropic thermal conductivity of few-layered BP samples at room temperature with micro-Raman spectroscopy. The measured armchair and zigzag thermal conductivities were about 20 and 40 W m\(^{-1}\) K\(^{-1}\) for BP samples thicker than 15 nm. They decreased to 10 and 20 W m\(^{-1}\) K\(^{-1}\) as BP thickness is reduced to 9.5 nm. Meanwhile, similar results were reported using the micro-bridge technique. Exfoliated BP samples were fabricated into nanoribbons along the armchair and zigzag directions with electron beam lithography (EBL). By bridging BP nanoribbons between two suspended pads, thickness and temperature dependence of the anisotropic thermal conductivity of BP were investigated. Jang et al. measured 138-552 nm BP samples with the time-domain thermoreflectance (TDTR) method. These BP samples were coated with a thin AlO\(_x\) layer to prevent oxidation. Thermal conductivities were 26-34 and 62-86 W m\(^{-1}\) K\(^{-1}\) in the armchair and zigzag directions at room temperature. Sun et al. further improved TDTR by studying bulk BP. It was reported that the armchair and zigzag thermal conductivities were 23-33 and 73-93 W m\(^{-1}\) K\(^{-1}\). Obviously, there is large inconsistency among these measurement results. The micro-Raman spectroscopy and the micro-bridge technique give similar measurement results, which are smaller than results obtained from TDTR method. These
results suggest our knowledge of BP’s thermal properties is still incomplete. Therefore, more studies are required to advance our understanding on thermal transport in BP.

1.2 Scope of Present Work

In this work, we continue to study thermal properties of BP with Raman spectroscopy. Previous researches have demonstrated compelling advantages of Raman spectroscopy over other techniques for thermal characterization, such as an easy sample preparation method, simple experimental procedures, and high spatial resolution. This work focuses on the measurement of interface thermal conductance and anisotropic thermal conductivity of BP. To achieve this goal, the crystalline orientation of BP must be identified firstly. The technique applied to identify the crystalline orientation must satisfy following requirements: First, it must be a nondestructive method so that BP samples can continue to be used for measuring their thermal properties. Second, it must be an in-situ method based on Raman spectroscopy. This can eliminate the oxidation of BP samples in the process of transferring between different instruments. Third, it must be able to identify the crystalline orientation of BP accurately regardless of sample thickness and excitation wavelength. To satisfy above requirements, a new technique, optothermal Raman spectroscopy (OT-Raman), is developed. OT-Raman utilizes anisotropic heating effect of a linear polarized laser on BP to identify its crystalline orientation. This reliable and robust technique lays the foundation for studies on thermal properties of BP.

Since Si is the most common substrate for fabricating and integrating device, it is worthful to study interface thermal conductance between BP and Si. In this work, thin BP samples are deposited on Si substrate, and their interface thermal conductance is measured with micro-Raman spectroscopy. By testing Si-supported BP samples with
various thickness at different temperature, thickness and temperature effect on interface thermal conductance can be explored. This study is the first experimental report for interface thermal conductance between BP and Si. It experimentally confirms the conclusion obtained from MD simulations that there is high interface thermal conductance between phosphorene (monolayer BP) and Si substrate. Furthermore, it suggests that BP is a promising interface material for next-generation devices.

The research on interface thermal conductance has exposed two major drawbacks of micro-Raman spectroscopy. First, it requires to evaluate absorbed laser power of BP samples. It has been suggested that accurate determination of absorbed laser power is very difficult. Second, it requires to calibrate Raman spectrum with temperature by measuring low-power-laser excited Raman spectrum at different temperature. Inaccurate results of absorbed laser power and calibration can lead to large measurement errors. To eliminate these measurement errors, frequency-resolved Raman spectroscopy (FR-Raman) is developed in our lab. This new technique enables thermal characterization even without the knowledge of absorbed laser power and calibration. The validity of this new technique is confirmed by measuring thermal diffusivity of a c-Si cantilever, which shows good agreement with literature-reported values. Then, FR-Raman is used to measure the armchair/zigzag thermal conductivity of suspended BP samples. Various suspended BP samples with different thickness are measured, which provides us insight into thickness effect on thermal transport along the BP plane.

These studies advance our fundamental understanding on phonon transport and interaction in black phosphorus, which can further benefit the development of new BP-based devices. Also, two newly developed techniques, OT-Raman and FR-Raman, has
demonstrated the versatility of Raman spectroscopy for studying material structure and measuring thermal properties. So far, these two techniques have shown great potential for studying other micro/nanomaterials. Especially for FR-Raman technique, we believe it will become an important tool for thermal characterization of micro/nanomaterials.
CHAPTER 2. PHYSICAL PRINCIPLES AND EXPERIMENTAL SETUP OF MICRO-RAMAN SPECTROSCOPY

Raman spectrum, which is commonly used to identify chemical molecules, has been used for probing local temperature rise due to its strong temperature dependence. This chapter introduces the development of micro-Raman spectroscopy for thermal characterization. Also, its physical mechanism and experimental setup are discussed thoroughly. As a technique used for developing OT-Raman and FR-Raman, this chapter provides us essential knowledge of micro-Raman spectroscopy, which can help us to understand OT-Raman and FR-Raman.

2.1 Development of Micro-Raman Spectroscopy

Micro-Raman spectroscopy is a reliable noncontact technique for probing local temperature rise with a high spatial resolution (~μm).\textsuperscript{28,29} For example, Beechem et al. reported the simultaneous mapping of temperature and stress distribution in doped polysilicon microheaters.\textsuperscript{30} Using a nanoscale near-field laser as a heating source, Yue et al. measured temperature rise of Si at a sub-10 nm scale.\textsuperscript{31} Moreover, Tang et al. investigated temperature rise and thermal stress in a nanoscale region of Si substrate beneath silica particles and glass fibers.\textsuperscript{32,33} The successful and reliable probing of local temperature rise with micro-Raman spectroscopy lays the foundation for applying this technique to measure thermal properties of micro/nanoscale materials. After the successful measurement of thermal conductivity of graphene by Balandin in 2008, micro-Raman spectroscopy has grown into a popular method to characterize thermal properties of two-dimensional materials.\textsuperscript{34} So far, the reliability and the versatility of micro-Raman spectroscopy have been demonstrated by charactering thermal properties of various two-
dimensional materials, such as thermal conductivity of TMDCs, \textsuperscript{35,36} and interface thermal conductance of graphene/Si, \textsuperscript{37} graphene/SiO\textsubscript{2}, \textsuperscript{37} MoS\textsubscript{2}/c-Si \textsuperscript{38}.

2.2 Physical Principles of Micro-Raman Spectroscopy

Raman spectrum is generated by irradiating a sample with a laser source. The characteristic fingerprint of Raman spectrum can be used for sample identification. Three parameters are typically used to describe Raman spectrum. They are intensity $I$ (the height of a Raman peak), wavenumber $\omega$ (the location of a Raman peak), and linewidth $\Gamma$ (the width of a Raman peak). The temperature-dependence of Raman spectrum is the physical foundation of micro-Raman spectroscopy for thermal characterization. To be specific, Raman spectrum has decreased intensity, redshifted wavenumber and broadening linewidth when temperature increases. In other words, temperature change can be monitored from the variation of intensity, wavenumber and linewidth. Typically, wavenumber is commonly used to monitor temperature change because it has a relatively high thermal sensitivity.

Micro-Raman spectroscopy uses an optical lens to focus a laser beam on a sample. The focused laser beam induces heating effect and excites Raman scattering simultaneously. Laser-induced local temperature rise can be probed from acquired Raman spectrum. The laser-induced heating effect can be adjusted by using various laser powers. Obviously, it can be enhanced when a large laser power is used. In terms of wavenumber, it moves to a low number region when excitation laser power becomes large. Typically, various laser powers are used to excite Raman spectra, so that the dependence of wavenumber on excitation laser power can be obtained. Such dependence, which has decreased wavenumber with increased laser power, can be described by its
slope, the wavenumber-power differential $\Phi$. $\Phi$ is determined accurately by fitting experimental data with a linear function. It is a measure of the change in wavenumber under the irradiation of a unit laser power. $\Phi$ is the key parameter of micro-Raman spectroscopy for thermal characterization.

The application of micro-Raman spectroscopy requires to calibrate Raman spectrum with temperature. The calibration involves the collection of Raman spectra at different temperature. It uses an extremely low laser power to excite Raman spectra in order to avoid additional laser-induced heating effect. This ensures the intrinsic temperature dependence of Raman spectrum on external temperature can be obtained. Temperature coefficient $\chi$ is used to characterize the variation of wavenumber with temperature. $\chi$ is the slope of the variation of wavenumber with temperature, which is determined by fitting experimental data with a linear function. It represents the change in wavenumber per degree temperature change. $\chi$ is the parameter used to convert the change in wavenumber into the change in temperature. To be specific, as a measure of average temperature rise under the irradiation of a unit incident laser power, $\partial \theta / \partial P$ is given by $\chi$ and $\Phi$ with the equation $\partial \theta / \partial P = \Phi / \chi$. $\partial \theta / \partial P$ is the parameter used directly to determine thermal properties. Based on the configuration of a studied system, theoretical values of $\partial \theta / \partial P$ can be calculated analytically or numerically when different values of thermal properties are assigned in our model. By comparing experimental $\partial \theta / \partial P$ with theoretical $\partial \theta / \partial P$, thermal properties can be eventually determined.

### 2.3 Experimental Setup

The experimental setup of our micro-Raman system is shown in Fig. 2.1 (a). An external 532-nm continuous-wave laser (Excelsior-532-150-CDRH Spectra-Physics) is
used as an energy source. It is linear-polarized with vertical polarization. Its polarization ratio is larger than 100:1. A half-wave plate is used to change laser polarization. The excitation laser power can be adjusted with a neutral density (ND) filter. After passing through the ND filter and the half-wave plate, the laser beam is reflected by several mirrors, and integrated into a microscope. Then, the laser beam is focused by a long working distance 20× objective. An environmental cell (HFS600E-PB4/PB2, Linkam Scientific Instruments) is used to house a BP sample. It is located under the 20× objective and on a 3D microstage (5 nm positioning resolution). The 3D microstage allows the irradiation of a focused laser beam on a specific spot of a BP sample precisely. This experimental setup collects Raman spectra in the backscattering configuration.

Figure 2.1 (b) and (c) show the top view and interior structure of the environmental cell. The top lid of the environemntal cell has a circular glass window. A laser beam can pass through the glass window and focused on a sample with negligible energy loss. The environmental cell has gas inlet/outlet to change the atmosphere in the cell chamber. Here, N₂ gas is used to purge air out of the chamber, and create an inert atmosphere which can prevent the degradation of a BP sample.³⁹-⁴² A sample is put on the pure silver heating/cooling block. A pair of heating wires can heat the pure silver block as high as 1100 K. A cooling tube is inserted into the pure silver block. Liquid N₂ can enter/leave the tube from the inlet/outlet. With liquid N₂ flowing through the tube, the pure silver block can be cooled as low as 80 K. The temperature can be adjusted precisely from 80 to 1100 K with a resolution of 1 K. The environmental cell is the most important instrument to obtain intrinsic Raman spectrum of BP at different temperature.
Figure 2.1 (a) Schematic of the micro-Raman system for thermal characterization. (b) Top view of the environmental cell. (c) Interior structure of the environmental cell.
CHAPTER 3. MECHANICAL EXFOLIATION OF BLACK PHOSPHORUS

Due to weak Van der Waals force between atomic layers and strong covalent bonds in each layer, a few-layered BP sample can be fabricated with mechanical exfoliation. In this work, few-layered BP samples are exfoliated from a bulk BP crystal, which was purchased from Smart Element and has a purity of ~99.998%, as shown in Fig. 3.1 (a). A modified mechanical exfoliation method is used to fabricate few-layered BP samples. In this modified method, the employment of viscoelastic stamps (PF-20/1.5-X4 Gelfilm from Gelpak) substantially increases the chance of obtaining large and uniform few-layered BP samples, and reduces sample contamination at the same time.

The modified mechanical exfoliation starts by pressing the bulk BP crystal gently against a viscoelastic stamp. After releasing the bulk crystal, many small crystallites are left on the surface of the viscoelastic stamp. Few-layered BP samples are exfoliated from these small crystallites. In practice, we choose a BP crystallite with a regular shape and a large thickness to do further mechanical exfoliation. Generally, a BP crystallite with a regular shape is a single crystal. A typical candidate BP crystallite perfectly suitable for mechanical exfoliation is shown in Fig. 3.1 (b). It has a rectangular shape with two natural-formed edges. A candidate BP crystallite can be picked up from rest crystallites with a viscoelastic stamp. This is achieved by pressing a new viscoelastic stamp on the surface of the viscoelastic stamp deposited with BP crystallites. When these two viscoelastic stamps are separated slowly, some BP crystallites can be transferred onto the new viscoelastic stamp completely. Such slow separation process ensures BP crystallites are not exfoliated. Then, we check these two viscoelastic stamps under a microscope to locate the candidate BP crystallite. The viscoelastic stamp containing the candidate BP
crystallite are kept for further separation. By repeating above separation process, we can eventually obtain a viscoelastic stamp with only the candidate BP crystallite deposited on it.

Few-layered BP samples are exfoliated from the candidate BP crystallite. It is achieved by pressing a new viscoelastic stamp on the candidate BP crystallite and releasing it rapidly. We have found that thick and regular-shaped BP crystallite are also suitable for continuous mechanical exfoliation. It means that many few-layered BP samples can be exfoliated from a single BP crystallite. This feature is important for the study of the crystalline orientation of BP. Once a few-layered BP sample is exfoliated, it is inspected under a microscope immediately. Its thickness can be estimated from its color contrast under normal illumination. Fig. 3.1 (c) shows the optical image of a few-layered BP sample. Its area with different thickness can be distinguished from different color contrast. For example, the thickness of the area with pale, purple and olive color are about 20, 75 and 85 nm, respectively. This phenomenon is a result of light interference in the thickness direction of the BP sample. An ideal few-layered BP sample must have a large lateral size and a uniform thickness. The strong color contrast makes it easy to identify an ideal sample rapidly under a microscope.

A few-layered BP sample deposited on a viscoelastic stamp can be transferred onto other substrate. This is achieved by simply putting the viscoelastic stamp in gentle contact with substrate and peeling it slowly with the aid of micro-manipulators. This operation is conducted under a microscope. A few-layered BP sample can be successfully transferred onto a Si substrate, a transmission electron microscopy (TEM) grid, and a square dent, as shown in Fig. 3.1 (d-f). The Si-supported BP sample can be used to study
the crystalline orientation of BP and thermal transport across the BP/Si interface. The one deposited on a TEM grid can be used to study the crystalline orientation of BP with TEM. The one suspended on a square dent can be used to study anisotropic in-plane thermal conductivity of BP. Figure 3.1 (f) shows the suspended area of BP can be distinguished easily from its surrounding supported area with its strong color contrast. The suspended area has a color of yellow, while its surrounding area has a color of green. After exfoliation and transfer, BP samples are kept in the environmental cell which is filled with N₂ gas. Since the total air-exposure time of these samples is less than 2 minutes, their oxidation in air is negligible.

Figure 3.1 (a) Optical image of the bulk BP crystal. (b) Optical image of a small BP crystallite deposited on a viscoelastic stamp. This BP crystallite is a single crystal. It has a large thickness. (c) Optical image of a few-layered BP sample deposited on a viscoelastic stamp. Its strong color contrast is thickness dependent. The thickness of the pale, purple and olive area is about 20, 75 and 85 nm, respectively. (d) Optical image of a BP sample deposited on Si substrate. (e) Optical image a BP sample on a TEM grid. (f) Optical image of a BP sample suspended on a square dent. The suspended area has different color contrast from its surrounding supported area.
CHAPTER 4. CRYSTALLINE ORIENTATION IDENTIFICATION WITH OPTOTHERMAL RAMAN SPECTROSCOPY

This chapter introduces optothermal Raman spectroscopy, which is a new technique to identify crystalline orientation of BP. Exfoliated BP samples supported on Si substrate are studied with optothermal Raman spectroscopy. This new technique utilizes the wavenumber-power differential $\Phi$ as an indicator to identify the crystalline orientation of BP. $\Phi$ has the largest value when laser polarization is in the armchair direction, while the smallest one when laser polarization is in the zigzag direction. This technique has a physical mechanism originated from the anisotropic heating effect of a linear polarized laser on BP. Our study has demonstrated the robustness and reliability of this technique for crystalline orientation identification regardless of excitation wavelength and sample thickness.

4.1 Previous Works for Identifying the Crystalline Orientation of BP

Although transmission electron microscopy (TEM) is the most straightforward technique to identify crystalline orientation, its application is limited due to its relatively complicated and challenging sample preparation procedures, especially for BP.\textsuperscript{14,20,44} Therefore, many new techniques have been developed for identifying the crystalline orientation of BP, such as polarization-resolved infrared spectroscopy,\textsuperscript{9} angle-resolved DC conductance,\textsuperscript{9} and angle-resolved polarized Raman spectroscopy (ARPRS).\textsuperscript{45} Among all these techniques, ARPRS is a widely used one due to its precise, simple and nondestructive features.\textsuperscript{10,17} First reported by Wu \textit{et al.}, ARPRS has demonstrated that $A_g^1$, $B_{2g}$ and $A_g^2$ mode have periodical variation in intensity as the rotation of a BP
sample under both paralleled- and cross-polarization configurations. This work concluded that the crystalline orientation of BP could be identified from intensity variation of $A_g^2$ mode under the paralleled-polarization configuration, which has the smaller local maximum intensity in the zigzag direction and the larger local maximum intensity in the armchair direction. This conclusion was confirmed by Ribeiro et al., who conducted similar angular Raman experiments using 633, 532, and 488 nm laser. However, further researches demonstrated that other factors such as excitation wavelength and sample thickness could also influence polarization dependence of intensity. Ling et al. discovered that the armchair direction and the zigzag direction couldn’t be distinguished explicitly from the periodic variation of intensity due to the influence of excitation wavelength and sample thickness. Such influence, as suggested by Kim et al., results from the optical interference in BP samples. These works definitely manifest that ARPRS is not capable of distinguishing between the armchair direction and the zigzag direction unambiguously unless excitation wavelength and sample thickness are considered carefully. Unlike ARPRS, OT-Raman utilizes the wavenumber-power differential $\Phi$ for crystalline orientation identification. The armchair direction and the zigzag direction can be easily identified and distinguished from the angular dependence of $\Phi$ on laser polarization regardless of excitation wavelength and sample thickness.
4.2 Experimental Results of OT-Raman

4.2.1 TEM and AFM Characterization on BP Samples

Our mechanical exfoliation method allows continuous exfoliation of few-layered BP samples from a single BP crystallite. Therefore, the crystalline orientation of one BP crystallite can be investigated by both OT-Raman and TEM. As the most straightforward technique for identifying crystalline orientation, TEM can verify the crystalline orientation identified by OT-Raman. This is a crucial step to verify the validity of OT-Raman. BP samples shown in Fig. 4.1 (a) and Fig. 4.2 (a) are indeed exfoliated from the same BP crystallite. They share exactly the same crystalline orientation due to their natural physical connection. Figure 4.1 (a) and (b) show the TEM image and its corresponding electron diffraction pattern of a thin BP sample. They demonstrate that [001] and [100] of the orthorhombic unit cell are along the armchair direction and the zigzag direction respectively. Meanwhile, the armchair/zigzag direction is normal/parallel to the nature-formed edge of the BP sample. 47

Figure 4.1 (a) TEM image of the BP sample supported on a TEM grid. The armchair/zigzag direction is normal/parallel to the nature-formed crystalline edge. (b) Electron diffraction pattern of the BP sample.
Figure 4.2 (a) Optical image of the BP sample deposited on Si substrate. The zigzag direction is along the x axis, and the armchair direction is along the y axis. $e_p$ represents the laser polarization vector. $\theta$ denotes the angle between the x axis and $e_p$. Four tested areas (a, b, c, and d) are marked by red stars. (b) AFM image of the BP sample. (c-f) Height profile along white lines in area a, b, c and d. Their thickness is 24.6, 32.7, 90.1 and 97.7 nm.

The TEM-identified crystalline orientation is labeled in the optical image of the BP sample, as shown in Fig. 4.2 (a). In the Cartesian coordinates, the zigzag direction is along the x axis, and the armchair direction is along the y axis. The vector $e_p$ represents laser polarization. The angle between $e_p$ and the zigzag direction is defined as $\theta$. The initial laser polarization is along the zigzag direction when $\theta$ is equal to 0°. Four areas with uniform color contrast marked by red stars are selected for OT-Raman experiments. They are characterized by atomic force microscope (AFM) after OT-Raman experiments. Figure 4.2 (b) gives the AFM image of the BP sample. Height profile along white lines in
the AFM image gives the thickness of a, b, c and d area, as shown in Fig. 4.2 (c-f). Their thickness is 24.6, 32.7, 90.1 and 97.7 nm, respectively. The roughness of BP surface results from their imperfect contact with Si substrate, slight oxidation of the sample as well as tiny amounts of PDMS residues.

**4.2.2 Basic Procedures and Principles of OT-Raman**

Here, we take the 24.6-nm BP sample as an example to demonstrate basic procedures and principles of OT-Raman. In an OT-Raman experiment, laser polarization is changed with a 20° angle step by rotating the half-wave plate. The total rotation of laser polarization is 360°. At each polarization angle, a BP sample is irradiated by various laser powers, from which the variation of Raman spectrum with laser power can be obtained. To avoid laser damage on a sample and excite sufficiently strong Raman signal, a precautions selection of appropriate laser powers is of great importance. For the 24.6-nm BP, laser powers irradiating on the BP surface are 7.69, 9.36, 11.65, 14.62, 19.54, 24.65, 28.94, 37.27 and 44.92 mW. Figure 4.3 (a) and (b) show Raman spectra excited by these laser powers when laser polarization is in the armchair/zigzag direction. These Raman spectra have been fitted by the Gaussian function. Three Raman peaks $A_g^1$, $B_{2g}$, and $A_g^2$ are located at 359, 436 and 464 cm$^{-1}$. Obviously, in these two cases of laser polarization, the relative intensity of $B_{2g}$ and $A_g^2$ modes change significantly, while that of $A_g^1$ remains almost unchanged. Most importantly, with increased excitation laser power, wavenumber of $A_g^1$, $B_{2g}$, and $A_g^2$ modes moves to a low number region.
Figure 4.3 Raman spectra of the 26.4-nm thick BP sample excited by different laser powers in the case of (a) armchair-polarization and (b) zigzag-polarization. These Raman spectra have been fitted by the Gaussian function. From the bottom spectrum to the top one, their corresponding excitation laser powers are 7.69, 9.36, 11.65, 14.62, 19.54, 24.65, 28.94, 37.27 and 44.92 mW, as shown by green arrows. Contour of the angular variation of wavenumber against laser power for (c) $A_g^1$ mode, (d) $B_{2g}$ mode, (e) $A_g^2$ mode.

For OT-Raman, the dependence of wavenumber ($\omega$) on excitation laser power plays a vital role for determining the crystalline orientation. Figure 4.3 (c-e) show contours of the angular variation of wavenumber of $A_g^1$, $B_{2g}$, and $A_g^2$ mode with excitation laser power. At each polarization angle, their wavenumbers have been normalized by their corresponding lowest-laser-power-excited wavenumber. These contours show wavenumber has an elliptical pattern with an elongation along the armchair direction. This suggests that a linear-polarized laser leads to the largest...
temperature rise when laser polarization is in the armchair direction. However, it can be found that these wavenumber contours, especially for the $A_{g}^{1}$ one, has large errors which makes it difficult to determine the crystalline orientation accurately. This makes us to use other parameter for crystalline orientation identification.

Instead of wavenumber ($\omega$), we have found that $\Phi$ is a more useful and reliable parameter for determining crystalline orientation accurately. As we can see in Fig. 4.4 (a), in both cases of the armchair-polarization and the zigzag-polarization, wavenumber ($\omega$) linearly depends on excitation laser power as $\omega=\omega_0+\Phi\cdot P$, where $\omega_0$ is the wavenumber at room temperature, and $\Phi$ is the linear slope. $\Phi$ of $A_{g}^{1}$, $B_{2g}$, and $A_{g}^{2}$ mode are $-0.0207 \pm 0.0023$, $-0.0376 \pm 0.0019$ and $-0.0413 \pm 0.0010$ cm$^{-1}$/mW in the armchair-polarization, while they are $-0.0113 \pm 0.0018$, $-0.0217 \pm 0.0015$ and $-0.0254 \pm 0.0024$ cm$^{-1}$/mW in the zigzag-polarization. Obviously, $\Phi$ in the armchair-polarization is always larger than that in the zigzag-polarization. The distinctively different $\Phi$ in the armchair- and zigzag-polarization allows us to determine the crystalline orientation. Figure 4.4 (b) shows $\Phi$ of these three Raman modes at different laser polarization angles. Apparently, they share exactly the same polarization dependence. Besides, they have the largest $\Phi$ in the armchair direction and the smallest one in the zigzag direction. $\Phi$ has a periodic pattern of 180°, which can be fitted by $\cos^2 \theta$ function nicely. The slight data dispersion can be attributed to several factors. They include the out-of-focus effect of a laser beam, the drift of a laser spot along the BP surface and the nonuniform physical contact between BP and Si substrate. Since $\Phi$ of these three Raman modes exhibit identical polarization dependence, anyone of them can be used to identify the crystalline orientation. Here, we choose the $A_{g}^{2}$ mode due to it has the largest $\Phi$ among all these
three Raman modes, as shown in Fig. 4.4 (b). The large $\Phi$ of $A_g^2$ mode will reduce data dispersion and improve the accuracy of crystalline orientation determination. In the following discussion, we will demonstrate that the polarization dependence of $\Phi$ originates from anisotropic optical absorption.

![Figure 4.4](image)

(a) The dependence of $A_g^1$, $B_{2g}$ and $A_g^2$ wavenumber on excitation laser power when laser polarization is in the armchair direction (red) and the zigzag direction (blue). These experimental data are fitted by a linear function. (b) Polar plot of $\Phi$ for $A_g^1$ (blue), $B_{2g}$ (green) and $A_g^2$ (red) modes. Experimental data are represented by dots, and theoretical fitting curves are represented by lines.

### 4.2.3 OT-Raman Performed on BP Samples with Different Thickness

To explore the BP-thickness influence on the polarization dependence of $\Phi$, BP areas with thickness of 26.4, 32.7, 90.1 and 97.7 nm (a, b, c, d) are studied. Their results are shown in Fig. 4.5 (a). As we have expected, they have an exactly same polarization-dependence of $\Phi$ with the largest (smallest) value in the armchair (zigzag) polarization. Generally, thick BP samples tend to have a larger $|\Phi|$. In total, 19 BP samples with different thickness are mechanically exfoliated from three BP crystallites and tested with OT-Raman. This thorough study proves the robustness of OT-Raman. The thinnest sample we have tested is 16.6 nm thick, and the thickest one is 282.7 nm thick. As
presented in Fig. 4.5 (b), $|\Phi|$ of both armchair- and zigzag-polarization ($|\Phi_{ac}|$ and $|\Phi_{zz}|$) increases with increased sample thickness, and $|\Phi_{ac}|$ is always larger than $|\Phi_{zz}|$. Defined as the ratio of $|\Phi_{ac}|$ to $|\Phi_{zz}|$, $\delta$ is used to quantitatively characterize the polarization dependence of $\Phi$ ($\delta=|\Phi_{ac}|/|\Phi_{zz}|$). The variation of $\delta$ against sample thickness is plotted in Fig. 4.5 (c). As shown by the blue guide line, the ratio $\delta$ oscillates with a damped amplitude as sample thickness increases. This oscillation results from the interference of the incident laser beam in BP samples. Detailed examination and discussion are given in the later-on sections. Since all the measured samples have $\delta$ much larger than 1, we can ascertain that $\Phi$ can be utilized for crystalline orientation identification at least for BP samples with a thickness up to 300 nm, and it has the great potential to be applied to much thicker samples.

Figure 4.5 (a) Polar plot of $\Phi$ for BP areas with thickness of 26.4 (blue), 32.7 (pink), 90.1 (red) and 97.7 (green) nm. Experimental data are represented with dots, and theoretical fitting curves are represented with lines. (b) The variation of $|\Phi_{ac}|$ and $|\Phi_{zz}|$ as a function of BP-thickness. Both $|\Phi_{ac}|$ and $|\Phi_{zz}|$ show a clearly increasing tendency. The error bars represent the standard error when experimental data are fitted by $\cos^2 \theta$ function. (c) The variation of $\delta$ ($|\Phi_{ac}|/|\Phi_{zz}|$) as a function of BP-thickness. Error bars represent the standard error. The blue line is used to guide eyes for the pattern of the $\delta$-thickness variation.
4.3 Physical Mechanism of OT-Raman

OT-Raman involves a complicated mechanism of optical absorption, heating, and thermal dissipation. When an incident laser beam irradiates the BP surface perpendicularly, both reflection and transmission happen at the air/BP interface. The transmitted part of laser beam will experience further alternate reflections at the BP/Si and BP/air interface. These multiple reflections in the BP layer can interfere destructively or constructively depending on the exact path length. The overall reflection from each interface is a sum of infinite number of reflections, and it can be described and calculated by the transfer matrix method (TMM). Fig. 4.6 (a) demonstrates optical reflection and transmission in the BP-Si bilayered structure. \( I_0 \) is the optical intensity of the incident laser beam, \( I_1 \) is the overall reflection intensity at the air/BP interface, \( I_2 \) is the overall reflection intensity at the BP/Si interface, and \( I_3 \) is the overall transmission intensity into Si substrate. Two key parameters in TMM for calculating \( I_1 \) and \( I_2 \) are the reflection index \( n \) and the extinction coefficient \( k \). Based on our literature reviews, the refractive index \( n \) is 3.02 in the armchair direction and 3.17 in the zigzag direction. Calculated from the absorption coefficient \( \alpha \) by the equation \( \alpha = 4\pi k/\lambda \), the extinction coefficient \( k \) is 0.216 and 0.135 in the armchair and zigzag directions. Current literatures have reported a large variation in \( \alpha \). Even in the same work, the calculated \( \alpha \) cannot agree well with the measured one. However, all the work agrees that the absorption coefficient \( \alpha \) in the armchair direction is larger than that in the zigzag direction. Our calculation of absorbance \( A \) based on \( n \) and \( k \) do have large uncertainty, but it can provide us basic idea of the evolution of \( A \) with laser polarization and BP thickness, which is essential and sufficient to explain the physical mechanism of OT-Raman.
First, we will demonstrate that $\Phi$ is proportional to $A$. Due to the anisotropic optical properties of BP, its volumetric optical absorption per unit time is expressed as $\dot{Q} = \dot{Q}_{ac} + \dot{Q}_{zz}$, where $\dot{Q}_{ac}$ and $\dot{Q}_{zz}$ are the volumetric optical absorption in the armchair direction and zigzag direction. $\dot{Q}_{ac}$ and $\dot{Q}_{zz}$ can be evaluated from following equations

$$\dot{Q}_{ac} = \sin^2 \theta \cdot \frac{I_1 e^{-z/\tau_{ac}} + I_2 e^{-h-z}/\tau_{ac}}{\tau_{ac}}, \quad (4.1)$$

$$\dot{Q}_{zz} = \cos^2 \theta \cdot \frac{I_1 e^{-z/\tau_{zz}} + I_2 e^{-(h-z)/\tau_{zz}}}{\tau_{zz}}, \quad (4.2)$$

where $\theta$ is the angle of laser polarization to the zigzag direction, $h$ is BP thickness, $\tau_{ac}$ and $\tau_{zz}$ are the penetration depth in the armchair and zigzag directions ($\tau = 1/\alpha = \lambda/4\pi k$). Then, the total absorbance $A$ in BP can be written as $A = \int_0^h (\dot{Q}_{ac} + \dot{Q}_{zz}) dz / I_0$, which leads to the equation,

$$A = (I_1 + I_2) \cdot \left[1 - \sin^2 \theta \cdot \exp(-h / \tau_{ac}) - \cos^2 \theta \cdot \exp(-h / \tau_{zz})\right] / I_0, \quad (4.3)$$

Optical absorbance $A$ is essential for unveiling the physical mechanism of OT-Raman. Its relationship to $|\Phi|$ can be established from thermal transport model. In this model, temperature distribution in BP is obtained from the following heat diffusion equation

$$k_{ac} \frac{\partial^2 T}{\partial x^2} + k_{zz} \frac{\partial^2 T}{\partial y^2} + k_\perp \frac{\partial^2 T}{\partial z^2} + \dot{Q}_{ac} + \dot{Q}_{zz} = 0, \quad (4.4)$$

where $k_{ac}$ is the armchair thermal conductivity, $k_{zz}$ is the zigzag thermal conductivity, and $k_\perp$ is the cross-plane thermal conductivity. The laser-induced heat in BP is dissipated along the BP plane ($Q_{in-plane}$) and across the BP/Si interface ($Q_{cross-plane}$), as shown in Fig. 4.6 (b). The steady temperature distribution is a result of competition between heat generation and thermal dissipation.
Figure 4.6 Optical transmission and reflection model of incident laser beam in BP-Si bilayer structure. To demonstrate light transmission and reflection clearly, the incident light is deliberately plotted non-normal to the BP surface. (b) Thermal transport model of laser-induced heat in BP. $Q_{\text{in-plane}}$ and $Q_{\text{cross-plane}}$ represent two approaches for dissipating thermal energy, in-plane thermal dissipation and across-interface thermal dissipation. The $z$ coordinate and its origin are labeled.

Since mathematical solving of equation (4.4) is impractical, the exact temperature distribution in BP remains unknown. However, we can still conclude that $T$ is proportional to $(\dot{Q}_{ac} + \dot{Q}_{zz})$ since equation (4.4) is a linear differential equation. As a result, we have $\bar{T} \propto Q_{ac} + Q_{zz}$, where $\bar{T}$ is the average temperature rise of the laser-irradiating area, and $Q_{ac} + Q_{zz}$ is the total laser absorption. Strictly speaking, such proportional relation works precisely for very thin BP samples (e.g. nm or tens of nm thickness), and it deviates gradually as BP thickness increases. However, for our analysis, such proportional relationship is accurate enough to study the crystalline orientation. The normalization of $\bar{T} \propto Q_{ac} + Q_{zz}$ by the total incident laser power $P$ leads to the expression $\partial \bar{T} / \partial P \propto A$, where $A$ is the absorbance we have mentioned before. Combined with the well-known equation $\partial T / \partial P = \Phi \cdot \chi^{-1}$ of micro-Raman spectroscopy, we have $\Phi \propto A \cdot \chi$, where $\chi$ is temperature coefficient. Considering the asymmetrical structure of BP, each P atom should also own an anisotropic potential which will further lead to polarization-
dependent \( \chi \). Previous work has reported the polarization dependence of \( \chi \), which is -0.02316 cm\(^{-1}\)K\(^{-1}\) in the armchair direction and -0.02700 cm\(^{-1}\)K\(^{-1}\) in the zigzag direction for a 9.5-nm thick BP sample. Note that the polarization dependence of \( \chi \) is contradictory to that of \( A \), and \( \chi \) will weaken the final anisotropy of \( \Phi \) contributed from \( A \). Here, we simply regard \( \chi \) as a constant due to their small difference in the armchair and zigzag directions. Then, the final expression relating \( \Phi \) and \( A \) is \( \Phi \propto A \). Figure 4.7 (a) presents the dependence of calculated \( A \) on laser polarization for BP samples with different thickness. Evidently, \( A \) has the maximum (minimum) value in the armchair (zigzag) direction, and it increases with increased thickness. The polarization dependence presented by our calculated \( A \) is same with the one obtained by microabsorption measurement. Therefore, the validity of \( \Phi \) as the indicator for identifying crystalline orientation can be explained very well by the consistency of \( A \)-dependence on the laser polarization.

### 4.4 Thickness Effect on OT-Raman

Let us now discuss in detail about \( \delta \) which characterizes the polarization dependence of \( \Phi \). As we mentioned above, the experimental \( \delta (\delta_e) \) is defined as the ratio of \( |\Phi_{ac}| \) to \( |\Phi_{zz}| \). From the optical absorbance \( A \) and its proportional relationship to \( \Phi \), the theoretical \( \delta (\delta_t) \) can be defined as \( A_{ac}/A_{zz} \). Compared with \( \delta_e \), \( \delta_t \) provides us more information about the change of \( \delta \) against thickness. As depicted in Fig. 4.7 (b), \( \delta_t \) decreases gradually and oscillates with a damped amplitude when sample thickness increases. In addition, when BP thickness is thicker than 1200 nm, the oscillation of \( \delta_t \) disappears and \( \delta_t \) is eventually saturated at 1, as shown in Fig. 4.7 (c). It indicates that the polarization dependence of \( A \) becomes weaker when sample thickness becomes thicker.
and there is a critical thickness from which the polarization dependence of $A$ becomes negligible. The oscillation is a result of destructive or constructive effect during the multiple laser reflection within BP samples. Although the amount of data $\delta_e$ is not high enough, we can still generally recognize its decreasing trend with a damped oscillation when sample thickness increases, which is similar to the change of $\delta_t$. The period of oscillation uncovered by experimental data is $\sim 74$ nm, which is close to $\sim 85$ nm that predicted by theoretical calculations. The smallest $\delta_e$ is $\sim 1.45$ for a 282.7-nm BP sample, and the largest one is $\sim 2.14$ for a 48.4-nm BP sample. Since $\delta_e$ is much larger than $\delta_t$, we can guarantee that OT-Raman is capable of identifying crystalline orientation for BP samples with thickness up to 300 nm at least. Also, we notice that $\delta_e$ and $\delta_t$ cannot agree well with each other and $\delta_e$ is larger than $\delta_t$ in most cases. The discrepancy between $\delta_e$ and $\delta_t$ can be caused by inaccurate measurement of $n$ and $k$ reported in literatures, the neglected anisotropic effect of $\chi$, as well as approximation used for the proportional relationship between $\Phi$ and $A$. Because it is out of the scope of this work, the influence of these factors on such discrepancy is not discussed. Nevertheless, we conclude that OT-Raman has a strong capability for identifying the crystalline orientation of BP samples as thick as 300 nm. The theoretical calculation further suggests that the thickness limitation for using OT-Raman can be as large as 1200 nm. No matter what the real thickness limitation is, the capability of OT-Raman is remarkable enough in typical research which studied BP samples are normally thinner than 100 nm.
Figure 4.7 (a) Polar plot of theoretical absorbance $A$ for BP samples with different thickness. $A$ has the maximum value in the armchair direction, and the minimum one in the zigzag direction. (b) The variation of $\delta_e$ and $\delta_t$ as a function of BP thickness. Experimental data $\delta_e$ are presented by black dots with error bars representing the standard deviation. The theoretical data $\delta_t$ are presented by a red line. The blue line is plotted to show the changing trend of $\delta_e$. Both $\delta_e$ and $\delta_t$ exhibit an oscillating behavior with a decreased amplitude against increased thickness. (c) The variation of $\delta_t$ in a thickness range up to 2000 nm.
CHAPTER 5. INTERFACE THERMAL CONDUCTANCE BETWEEN MECHANICALLY EXFOLIATED BLACK PHOSPHORUS AND SI SUBSTRATE

In this chapter, thermal transport across BP/Si interface are studied with micro-Raman spectroscopy. This study is performed on few-layered BP samples deposited on Si substrate. Totally, eight BP samples with thickness of 16.6, 26.4, 33.1, 39.4, 48.4, 75.7, 82.1, and 113.7 nm are studied in a temperature range of 223 to 293 K. The crystalline orientation of these samples is identified with OT-Raman before measuring their interface thermal conductance. The laser polarization is aligned along the armchair direction to keep the consistency of experiments performed on different BP samples. This study allows us to explore thickness effect and temperature effect on interface thermal conductance. This research suggests BP is a very promising interface material for future devices.

5.1 Basic Procedures and Principles of Measurement

As the thinnest BP sample that we have studied so far, the 16.6-nm thick BP sample is taken as an example to demonstrate how interface thermal conductance can be measured. The optical image of the 16.6-nm BP sample is shown in Fig. 5.1 (a). Its crystalline orientation identified with OT-Raman is labeled in the figure. The area with faint color contrast (squared by white dashed lines) has the thinnest thickness. The AFM image and its corresponding height profile along the white line gives the accurate thickness of the thinnest area, which is 16.6 nm, as shown in Fig. 5.1 (b) and (c). The surface roughness observed in Fig. 5.1 (c) results from micro-wrinkles and oxidation bubbles.41,42,49
Figure 5.1  (a) Optical image of the BP sample. The crystalline orientation is labeled as AC and ZZ to represent the armchair direction and the zigzag direction. The thinnest area, squared by white dashed lines, has weak color contrast. (b) AFM image of the BP sample. (c) Height profile along the white line in the AFM image. It gives thickness and roughness of the thinnest area. The height profile clearly shows the thinnest area has a thickness of 16.6 nm.

The 16.6-nm area is irradiated with a laser beam to obtain its Φ. Here, we emphasis again that laser polarization is aligned along the armchair direction, and laser powers must not damage the BP sample when evident temperature rise is induced. For the 16.6-nm area, laser powers irradiating on the sample surface are 9.61, 11.69, 14.57, 18.27, 24.42, 30.81, 36.18, 46.58, and 56.15 mW. Their corresponding Raman spectra excited at 293 K are shown in Fig. 5.2 (a). These Raman spectra have been fitted with Gaussian function to show their variation with laser power clearly. Obviously, wavenumber has redshift due to enhanced heating effect when laser power increases. These accurate values of wavenumber obtained from Gaussian-function fitting are plotted in Fig. 5.2 (b). The variation of wavenumber against laser power shows a strong linearity.

For $A_{1g}^1$, $B_{2g}$, and $A_{g}^2$ mode, their Φ are $-0.0186 \pm 0.0032$, $-0.0300 \pm 0.001$, and $-0.0323 \pm 0.0013$ cm$^{-1}$mW$^{-1}$, respectively. Once again, the largest value of Φ of the $A_{g}^2$ mode proves the $A_{g}^2$ mode has the largest temperature sensitivity. The $A_{g}^2$ mode is used to conduct following analysis.
Figure 5.2 (a) Gaussian-fitted Raman spectra of the 16.6-nm BP sample excited by a laser with powers between 3.64 and 21.27 mW at 293 K. (b) The variation of wavenumber of $A_g^1$, $B_{2g}$, and $A_g^2$ mode with laser power at 293 K. Their $\Phi$ are $-0.0186 \pm 0.0032$, $-0.0300 \pm 0.001$, and $-0.0323 \pm 0.0013$ cm$^{-1}$/mW. (c) The variation of wavenumber of the $A_g^2$ mode as a function of laser power in a temperature range of 223 to 293 K. These wavenumbers excited with the lowest laser power are shadowed with red color. The lowest laser power is 9.61 mW. (d) The variation of $\Phi$ as a function of temperature. Error bars give the standard deviation of $\Phi$. (e) The temperature dependence of wavenumber obtained from Raman spectra excited with the 9.61-mW laser. Its slope $\chi$ is equal to $-0.0264 \pm 0.0012$ cm$^{-1}$K$^{-1}$.

Same measurement is repeated at 223, 233, 243, 253, 263, 273, and 283 K. Then, the variation of wavenumber of the $A_g^2$ mode with laser power from 223 to 293 K are obtained and presented in Fig. 5.2 (c). They all show a strong linearity. Their
corresponding $\Phi$ obtained by linear fitting are plotted in Fig. 5.2 (d). Obviously, $\Phi$ has an increasing tendency when temperature decreases. To calculate $\partial \theta / \partial P$ from $\Phi$, temperature coefficient $\chi$ is indispensable. In this case, wavenumbers obtained from Raman spectra excited with the lowest laser power 9.61 mW can be used to determine $\chi$. They are shadowed with red color in Fig. 5.2 (c) and plotted in Fig. 5.2 (e). They show strong linearly dependence on temperature. The linear fitting to these data gives the value of $\chi$, which is equal to $-0.0264 \pm 0.0012$ cm$^{-1}$K$^{-1}$. This value of $\chi$ can be regarded as an intrinsic one since the 9.61-nm laser has negligible heating effect.

### 5.2 Determination of Interface Thermal Conductance

With determined $\Phi$ and $\chi$, $\partial \theta / \partial P$ can be calculated with the equation $\partial \theta / \partial P = \Phi \chi$.

For the 16.6-nm BP sample, its $\partial \theta / \partial P$ from 223 to 293 K are shown in Fig. 5.3 (a). From 223 to 293 K, $\partial \theta / \partial P$ increases from $\sim 0.8$ to $\sim 1.2$ K/mW. As a parameter characterizing the average temperature rise under the irradiation of a unit laser power, the theoretical value of $\partial \theta / \partial P$ can be calculated by simulating the studied system with an appropriate thermal transport model. For a simple description, the experimental $\partial \theta / \partial P$ is defined as $(\partial \theta / \partial P)_e$, and the theoretical $\partial \theta / \partial P$ is defined as $(\partial \theta / \partial P)_m$.

Our studied system has a bilayer structure, which consists of a BP layer and a Si layer. The BP layer is under the direct irradiation of a laser beam. The laser energy absorbed by the BP layer is dissipated through the BP plane and across the BP/Si interface simultaneously. However, cross-plane thermal transport takes the major role for dissipating heat. Thus, the anisotropy of the in-plane thermal conductivity of BP can be neglected by approximating the in-plane thermal conductivity as the average of armchair thermal conductivity and zigzag thermal conductivity. The Si layer acts as a heating sink,
which remains at a constant temperature. The thermal response of the studied system to a focused laser beam is given by following equations \(21\)

\[
\kappa_r \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \theta}{\partial r} \right) + \kappa_\perp \frac{\partial^2 \theta}{\partial z^2} + \dot{Q} = 0, \tag{5.1}
\]

\[
\dot{Q} = \frac{I_1}{\tau} e^{-z/\tau} + \frac{I_2}{\tau} e^{-(h-z)/\tau} e^{-r^2/h_0^2}, \tag{5.2}
\]

where \(\kappa_r\) is the in-plane thermal conductivity with a value of 30 Wm\(^{-1}\)K\(^{-1}\). It is calculated by averaging the armchair thermal conductivity (20 Wm\(^{-1}\)K\(^{-1}\)) and the zigzag thermal conductivity (40 Wm\(^{-1}\)K\(^{-1}\)). \(10\) \(\kappa_\perp\) is the through-plane thermal conductivity which is equal to 4 Wm\(^{-1}\)K\(^{-1}\). \(17\) \(\dot{Q}\) is volumetric optical absorption per unit time when laser polarization is in the armchair direction. In the expression of \(\dot{Q}\), \(r_0\) is the radius of the laser spot which is equal to 1.28 \(\mu\)m, \(h\) is BP thickness, \(\tau\) is the penetration depth when laser polarization is in the armchair direction, \(I_1\) and \(I_2\) is the overall reflection intensity at the air/BP interface and BP/Si interface, as shown in Fig. 4.6 (a). \(I_1\) and \(I_2\) are calculated using TMM method (described in Chapter 4) with the armchair-direction refractive index \((n_{ac})\) and the armchair-direction extinction coefficient \((k_{ac})\). \(21,38\) In the case of 532-nm laser illumination, we know that \(n_{ac} = 3.02\) and \(k_{ac} = 1.39\). \(15\) A three-dimensional numerical modeling based on the finite difference volume method is conducted to solve the equation (5.1). It gives us three-dimensional temperature distribution in the BP layer.

As we have mentioned before, \((\partial \theta / \partial P)_e\) represents the average temperature rise under the irradiation of a unit laser power. However, the term “the average temperature rise” is not accurate enough. In fact, the temperature rise obtained from Raman spectra is an average in space weighted by local Raman intensity. \(21\) So, the accurate term is “the
Raman-intensity weighted average temperature rise. We can calculate the Raman-intensity weighted average temperature rise $\theta_m$ from temperature distribution with following equations,

$$\theta_m = \Theta / \Pi , \quad (5.3 \text{a})$$

$$\Theta = \int_0^\delta \int_0^\infty \theta(r) \exp(-r^2 / \tau_0^2) \left[ I_1 \exp(-z / \tau) \gamma_1 + I_2 \exp(-z / \tau) \gamma_2 \right] r dr dz , \quad (5.3 \text{b})$$

$$\Pi = \int_0^\delta \int_0^\infty \exp(-r^2 / \tau_0^2) \left[ I_1 \exp(-z / \tau) \gamma_1 + I_2 \exp(-z / \tau) \gamma_2 \right] r dr dz , \quad (5.3 \text{c})$$

in which $\theta(r)$ is temperature distribution obtained from the equation (5.1), $\gamma_1$ and $\gamma_2$ are coefficients of the attenuation of Raman signal generated at a location of $r$ and $z$. $\theta_m$ is determined with numerical simulations. $\theta_m$ is equal to $(\partial \theta / \partial P)_m$ when the simulation is conducted with the incident laser power set as 1 mW.

An example of numerical simulations is shown in Fig. 5.3 (b) and (c). The contour in Fig. 5.3 (b) gives the simulated temperature distribution in the 16.6-nm BP sample and its adjacent Si substrate at 293 K. Figure 5.3 (c) shows temperature rise of the BP bottom surface and the Si top surface. It can be observed that the Si top surface has small temperature rise compared with the BP bottom surface. The Raman-intensity weighted average temperature rise of Si is 0.46 K mW$^{-1}$, agreeing well with the measured one which is 0.58 K mW$^{-1}$. These results suggest that there is large temperature difference on the BP/Si interface. They are obtained by specifying a value for thermal resistance $R$. From the simulated temperature distribution in the BP layer, $(\partial \theta / \partial P)_m$ can be determined. By changing the setting value of thermal resistance $R$, we can have the variation of $(\partial \theta / \partial P)_m$ as a function of $R$. For the 16.6-nm BP sample, its $(\partial \theta / \partial P)_m$ is plotted against $R$ in Fig. 5.3 (d). $(\partial \theta / \partial P)_m$ has a linear dependence on $R$. By interpolating
\((\partial \theta / \partial P)_e\) [Fig. 5.3 (a)] into the curve of \((\partial \theta / \partial P)_{m}\) [Fig. 5.3 (d)], thermal resistance \(R\) at different temperature can be determined. Since \(G\) is the reciprocal of \(R\), \(G\) is calculated from \(R\) and plotted in Fig. 5.3 (e). \(G\) tends to increase when temperature decreases. \(G\) is 36.2 MWm\(^{-1}\)K\(^{-1}\) at 293 K, and it increases to 82.7 MWm\(^{-1}\)K\(^{-1}\) at 223 K. This suggests that low temperature can facilitate thermal transport across the BP/Si interface.

**Figure 5.3** (a) The variation of \((\partial \theta / \partial P)_e\) as a function of temperature. Error bars give the standard deviation of \((\partial \theta / \partial P)_e\). (b) Contour mapping of temperature distribution in BP and its adjacent Si at 293 K. (c) Temperature rise of the BP bottom surface and the Si top surface. (d) The variation of \((\partial \theta / \partial P)_{m}\) with thermal resistance \(R\). \((\partial \theta / \partial P)_{m}\) shows a strong linear dependence on \(R\). (e) Interface thermal conductance \(G\) at different temperature. \(G\) tends to increase with decreased temperature. \(G\) is 36.2 MWm\(^{-1}\)K\(^{-1}\) at 293 K, and 82.7 MWm\(^{-1}\)K\(^{-1}\) at 223 K.

**5.3 Results and Discussion**

In this work, BP samples with thickness of 16.6, 26.4, 33.1, 39.4, 48.4, 75.7, 82.1 and 113.7 nm are tested thoroughly from 223 to 293 K. Their interface thermal
conductance $G$ are presented in Fig. 5.4. Generally, $G$ increases as temperature decreases. So far, Zhang et al. reported MD simulations of interface thermal conductance between monolayer BP and Si, which is about 67 MWm$^{-2}$K$^{-2}$ at 300 K. This value is indeed very close to our experimental results. The explanation of Zhang et al. is accepted to understand the high $G$ of the BP/Si interface. The large overlap of PDOS (phonon density of state) of BP and its adjacent Si leads to the formation of a strong phonon coupling between these two materials. It indicates that more phonons are involved in thermal transport across the BP/Si interface. As a result, the BP/Si interface owns a high $G$. However, temperature dependence of $G$ obtained by MD simulations is contradictory to our experimental results. By assuming a perfect contact between monolayer BP and its adjacent Si, MD simulations demonstrated that $G$ decreases with decreased temperature due to the temperature-dependent variation of the PDOS overlap. However, according to literature review, we found that our observed temperature-dependence of $G$ is identical to that of Taube et al. Taube et al. showed that interface thermal conductance between a single layer of MoS$_2$ and it adjacent SiO$_2$/Si substrate has an increasing tendency with decreased temperature. Despite they didn’t provide any explanation to this phenomenon, their results help to exclude causes of this anomalous phenomenon from measurement mistakes and experimental artifacts.

Currently, we believe the morphological variation of the BP/Si interface with temperature should be responsible for the temperature-dependence of $G$. In a natural state, exfoliated BP samples are attached on Si substrate imperfectly with micro/nanoscale wrinkles and ripples. The existence of these micro/nanoscale wrinkles and ripples makes $G$ smaller than it should be. However, interface contact can be
improved by decreasing temperature. This is induced by the unequal thermal expansion coefficient of BP and Si. The thermal expansion coefficient of BP is larger than Si.\textsuperscript{21,23,50} In other words, a free-standing BP sample will have a larger contraction than Si at low temperature. However, for a BP sample attached on Si substrate, its contraction is restricted due to the strong Van der Waals force between BP and Si when temperature decreases. It leads to the accumulation of tensile strain along the BP plane, which can improve the interface contact by flattening micro-wrinkles and ripples. As a result, $G$ becomes larger at low temperature.

Also, we try to unveil the relationship between $G$ and BP thickness. In fact, $G$ is intimately related to interface characteristics, such as contact condition, atomic bonding, and phonon coupling.\textsuperscript{51,52} Thus, any factors that can influence interface characteristics directly or indirectly will result in the change of $G$. However, no clear thickness dependence of $G$ can be identified at this time. As shown in Fig. 5.4, the 82.1-nm thick sample and the 26.4-nm thick sample have interface thermal conductance deviating from rest samples dramatically. From 223 to 293 K, the 82.1-nm thick sample has the largest $G$, while the 26.4-nm thick one has the smallest one. In addition, the 82.1-nm thick sample and the 75.7-nm thick sample have large difference in $G$ even though their thickness difference is small. In fact, the 82.1-nm thick sample has $G$ several times larger than that of the 75.6-nm thick sample. Currently, we belief this is relevant to the morphological characteristics of BP samples, which is highly sample-dependent. The sample-related morphological variation can be large enough to completely overshadow the intrinsic dependence of $G$ on BP thickness. As a result, more investigations are required to discover the relationship between $G$ and BP thickness.
Figure 5.4 Interface thermal conductance $G$ of BP samples with different thickness measured at 223 to 293 K. Their thicknesses are labeled clearly. Error bars show the measurement uncertainty of $G$.

### 5.4 Measurement Errors of Interface Thermal Conductance

Measurement errors of $G$ are analyzed carefully in this section. One factor can influence measurement accuracy is oxidation of BP in air. Oxidation occurring in the process of sample preparation and transfer is negligible. Thus, oxidation has negligible effect on acquired Raman spectra. However, oxidation happens on BP samples when they are characterized by AFM to determine their thickness after acquiring Raman spectra. The AFM characterization is conducted in air, so that oxidation of BP is inevitable. By absorbing moisture and oxygen, oxidation bubbles form randomly on BP surface. These oxidation bubbles can be identified easily from an AFM image. These white dots in Fig. 5.1 (b) are indeed oxidation bubbles. With a height larger than its surrounding area, oxidation bubbles can also be recognized easily from the height profile of an AFM image. Therefore, thickness error can be minimized by interpreting the height profile of an AFM image seriously. Although thickness is determined with great carefulness, its
error is still not avoidable due to surface roughness. Here, the thickness-related measurement error of $G$ are calculated when the standard deviation of thickness is 2 nm. Additionally, $\Phi$ and $\chi$ are other two factors that can induce large measurement errors. Their errors are induced by effects like the laser spot drift along sample surface and the out of focus of a laser beam. From the standard deviation of $\Phi$ and $\chi$, their corresponding contribution to measurement errors of $G$ can be calculated. Combined measurement errors of $G$ resulting from thickness, $\Phi$, and $\chi$ are calculated and represented with error bars in Fig. 5.4. As shown in Fig. 5.4, $G$ measured from different BP samples shows a wide dispersion, which is much larger than measurement errors. Considering our mechanical method for sample preparation, this phenomenon can only result from the large variation in the physical contact on the BP/Si interface.

In our thermal transport model, Si substrate is assumed to be pristine without any native oxide. However, once pure Si is exposed to air, there is a thin layer of oxide building on its surface rapidly. The stoichiometry and morphology of this oxide layers are not fully understood yet. Previous studies suggested that the oxide layer is amorphous with a thickness of ~2 nm. Here, $\text{SiO}_x$ is used to represent the thin layer of oxide capping on Si surface. The influence of $\text{SiO}_x$ on $G$ is considered rigorously. Due to the existence of $\text{SiO}_x$, thermal resistance between BP and pure Si ($R_{BP/Si}$) is revised as $R_{BP/Si} = R_1 + R_2$, where $R_1$ is thermal resistance between BP and $\text{SiO}_x$, and $R_2$ is thermal resistance of $\text{SiO}_x$. $R_2$ is equal to $l/k$, where $l$ is thickness of $\text{SiO}_x$ and $k$ is thermal conductivity of $\text{SiO}_x$. As a transition between crystalline silicon and amorphous silicon dioxide, $\text{SiO}_x$ has unknown thermal conductivity. Here, we assume that thermal conductivity of $\text{SiO}_x$ is equal to thermal conductivity of amorphous silicon dioxide. \cite{55}
This assumption provides us the lower limit of thermal conductivity of SiO$_x$. $R_2$ is estimated as $1.45 \times 10^{-9}$ m$^2$ K W$^{-1}$ when $l=2$ nm and $k=1.38$ W m$^{-1}$ K$^{-1}$. Note, $R_2=1.45 \times 10^{-9}$ m$^2$ K W$^{-1}$ is the upper limit value. If $R_2$ is much smaller than $R_{BP/Si}$ and $R_1$, it can be neglected. BP samples has thermal resistance much larger than $R_2$ except the 82.1-nm thick sample. In other words, $R_2$ becomes negligible except the 82.1-nm thick BP sample.

As shown in Fig. 5.4, the 82.1-nm thick sample has $G$ deviating from rest samples significantly. The reason of such large deviation is still unclear, more studies are required to answer this question.
CHAPTER 6. DEVELOPMENT OF FREQUENCY-RESOLVED RAMAN SPECTROSCOPY FOR THERMAL CHARACTERIZATION

This chapter introduces the development of frequency-resolved Raman spectroscopy (FR-Raman) for thermal characterization. This technique is performed on a c-Si cantilever to measure its thermal diffusivity. Thermal diffusivity is determined as 9.57×10⁻⁵ m²/s, 11.00×10⁻⁵ m²/s and 9.02×10⁻⁵ m²/s from intensity, wavenumber and total Raman emission. These results are in good agreement with the reference value of thermal diffusivity of c-Si, which verifies the validity of this new technique.

6.1 Physical Principles of Frequency-resolved Raman Spectroscopy

Physical principles of FR-Raman are illustrated in Fig. 6.1 (a). FR-Raman utilizes a square-wave modulated laser to induce heating effect and excite Raman scattering. In each period of a modulated laser, there are a laser-on time τₜ and a laser-off time τₖ (τₚ is always equal to τₜ). Under the irradiation of a modulated laser, a sample experiences alternate heating and cooling, which can reach a steady periodic thermal state at last. At a steady periodic thermal state, temperature rise during τₜ is equal to temperature drop during τₚ, as shown in Fig. 6.1 (a). During each period of τₜ, increased temperature leads to the change in instantaneous Raman scattering, which has decreased intensity (I), redshift wavenumber (ω), and broadening linewidth (Γ). In fact, the variation in intensity, wavenumber and linewidth closely follows the change in temperature. All the Raman scattering excited during τₜ is acquired. The acquired Raman spectrum is related to the average temperature rise $\bar{\theta}$ during τₜ.

The average temperature rise $\bar{\theta}$ during τₜ is modulation-frequency (f) dependent. In general, a modulated laser has enhanced heating effect as f decreases. Heating effect of
a modulated laser at a very high and low \( f \) are two extreme cases, as shown in Fig. 6.1 (b) and (c). At a very high \( f \), temperature variations during \( \tau_h \) and \( \tau_c \) are so small that temperature can be regarded as a constant. This state is defined as the “quasi-steady state” with an average temperature rise \( \overline{\theta}_{qs} \) during \( \tau_h \) (\( \overline{\theta}_{qs} \) is equal to \( T_{qs} - T_0 \)). At a very low \( f \), temperature increases from the initial temperature \( T_0 \) and converges to its steady state temperature \( T_s \) during \( \tau_h \), while it decreases from \( T_s \) and returns \( T_0 \) during the following \( \tau_c \). This state is defined as the “steady state” with an average temperature rise \( \overline{\theta}_s \) during \( \tau_h \) (\( \overline{\theta}_s \) is equal to \( T_s - T_0 \)). In the “steady state”, we neglect the short transient period during which temperature increases from \( T_0 \) to \( T_s \). In fact, the thermal response to a low-\( f \) modulated laser during \( \tau_h \) is identical to the thermal response to a continuous-wave laser. From a high \( f \) to a low \( f \), the thermal response varies from the “quasi-steady state” to the “steady state” gradually. Their corresponding average temperature rise \( \overline{\theta} \) increases from \( \overline{\theta}_{qs} \) to \( \overline{\theta}_s \). Our previous work has rigorously proved that \( \overline{\theta}_{qs} = \overline{\theta}_s / 2 \). \(^{27}\) In addition to modulation frequency \( f \), \( \overline{\theta} \) is also a function of absorbed laser power and thermal properties of the studied system. Once \( \overline{\theta} \) is normalized by \( \overline{\theta}_s \), we have the normalized average temperature rise \( \overline{\theta}_{nor} \), which is a dimensionless quantity representing the relative temperature variation. \( \overline{\theta}_{nor} \) varies from 1/2 to 1 when \( f \) decreases. Such \( f \)-dependent variation in \( \overline{\theta}_{nor} \) is only determined by thermal properties of the studied system.
Figure 6.1 (a) Physical principles of FR-Raman. A modulated square-wave laser is used as an energy source to heat a sample. A sample experiences alternate heating and cooling, which can eventually reach a steady periodic thermal state. The temperature evolution during $\tau_h$ leads to corresponding change in instantaneous Raman scattering. During each period of $\tau_h$, as temperature increases, instantaneous Raman scattering has decreased intensity, redshifted wavenumber and broadening linewidth. (b) Periodic temperature variation at the “quasi-steady” state when modulation frequency is very high. Its average temperature rise $\bar{\theta}_{qs}$ during $\tau_h$ is equal to $T_{qs} - T_0$. (c) Periodic temperature variation at the “steady state” when modulation frequency is very low. Its average temperature rise during $\tau_h$ is equal to $T_s - T_0$.

In a FR-Raman experiment, the variation of $\bar{\theta}_{nor}$ with $f$ can be obtained from the variation of Raman spectrum with $f$. Again, we emphasize that temperature dependence of Raman spectrum enables us to monitor the variation of $\bar{\theta}_{nor}$ with $f$. To extract thermal properties of a studied system, an equation that can describe theoretical thermal transport in the studied system is required. This equation takes studied thermal properties as
unknown parameters. Therefore, by fitting experimental data of $\bar{\theta}_{\text{nor}}$ with our derived equation, studied thermal properties can be determined ultimately. The first FR-Raman experiment is performed on a c-Si cantilever to measure its thermal diffusivity. c-Si has well studied thermal diffusivity. Therefore, by comparing our measured thermal diffusivity with other literature reports, the validity of this new technique can be confirmed.

6.2 Experimental Details of FR-Raman Performed on a Si Cantilever

The experiment is performed on a c-Si cantilever (AppNano, Ltd) in open air at room temperature (293K). Figure 6.2 (a) shows the top view of the c-Si cantilever. The c-Si cantilever extends from a Si chip and has a triangular tip end. The length $L$, width $w$ and thickness $\delta$ of the c-Si cantilever is 450.35 $\mu$m, 49 $\mu$m and 2.5 $\mu$m, respectively. The c-Si cantilever has a triangular end with a height $h$ of 22.95 $\mu$m. A 532-nm continuous-wave (CW) laser (MSL-III-532-AOM-150mW, Ulralaser, Inc) is used as an energy source. This CW laser can be modulated into a square waveform using a function generator (DS345). The rise time of a pulse in the modulated laser is 130 ns. The modulated laser beam is focused by a 4× objective lens to a spot size of 31.4×65.3 $\mu$m$^2$. The laser beam used to irradiate the c-Si cantilever has a power of 7.9 mW before modulation. This low laser power can heat the c-Si cantilever without inducing large thermal stress and damaging the sample. Since the c-Si cantilever is placed on a 3D microstage, the laser spot can be focused on the c-Si cantilever tip precisely. The integration time for acquiring Raman spectra is 15 s. This ensures these acquired Raman spectra can have a high signal-to-noise ratio. A modulation frequency range from 100
kHz to 17 Hz is broad enough to induce thermal response from the “quasi-steady state” and to the “steady state”. Figure 6.2 (b) gives several Raman spectra excited at different modulation frequency. The characteristic Raman peak of c-Si is located at 520 cm\(^{-1}\).

Figure 6.2  (a) *The optical image of the c-Si cantilever. The green square gives the laser irradiating area. The heating area on the c-Si cantilever is marked by red dash lines.* (b) *Raman spectra of the c-Si cantilever excited by a modulated laser with different modulation frequency.*

The contour in Fig. 6.3 (a) shows all acquired Raman spectra excited by a modulated laser with frequency between 17 Hz to 100 kHz. This gives an overall picture on the evolution of Raman spectrum with modulation frequency. These accurate values of intensity, wavenumber and linewidth are obtained by fitting these Raman spectra with Gaussian function. They are plotted against modulation frequency (\(f\)) in Fig. 6.3 (b). As shown in Fig. 6.3(b), Raman spectrum has increased intensity and redshift wavenumber when modulation frequency increases. Unlike intensity and wavenumber, with a relatively low signal-to-noise ratio, linewidth decreases with increased modulation frequency. The variation of intensity, wavenumber and linewidth against modulation frequency (\(f\)) are used to extract thermal diffusivity. How fast or slow these Raman parameters change from the “steady state” to the “quasi-steady state” is determined by
thermal diffusivity of c-Si. To extract thermal diffusivity of c-Si, a physical model is developed to describe thermal transport of the c-Si cantilever.

![Image](image.png)

Figure 6.3 (a) Contour mapping of Raman spectra excited by a modulated laser with frequency between 17 Hz to 100 kHz. (b) The variation of intensity, wavenumber and linewidth against modulation frequency.

### 6.3 Physical Model of Thermal Transport

When the tip of the c-Si cantilever is irradiated by a laser beam, the Si chip acts as a thermal sink, which remains at room temperature (293 K), for dissipating heat generated on the c-Si cantilever tip. Thermal transport from the c-Si cantilever tip to the Si chip can be described by one-dimensional heat conduction. Heat conduction in the thickness direction is neglected since the thickness is relatively small compared with the length. Also, heat conduction in the width direction is neglected since the width of the focused laser spot is larger than the width of the c-Si cantilever. The shape of the c-Si cantilever is refined to simplify thermal transport model. The original triangular tip is simplified as a rectangular tip in our model. The area of the new tip is same to that of the original triangular tip, which ensures they have same laser-irradiating area. The length of
the shape-refined c-Si cantilever is 438.88 μm (l=L-h/2). The laser-irradiating area is between \(x_1\) (418.95 μm) and \(x_2\) (438.88 μm), as shown in Fig. 6.2 (a).

The modeling of thermal response to a modulated laser is complicated and time-consuming. However, it can be obtained indirectly from thermal response to a step-wave laser using the superposition law of a linear differential function (heat conduction is a linear differential function). Therefore, we obtain the solution of heat conduction when a step-wave laser is an energy source. This solution, then, is used to construct the solution of heat conduction when a modulated laser is an energy source. With a step-wave laser as an energy source, heat conduction along the c-Si cantilever is given by

\[
\rho c_p \frac{\partial \theta}{\partial t} = k \frac{\partial^2 \theta}{\partial x^2} + \dot{Q},
\]

where \(\dot{Q}\) is the volumetric optical absorption per unit time, and \(\theta, \rho, c_p\) and \(k\) are temperature rise, density, specific heat, and thermal conductivity of c-Si, respectively. Green function is used to solve the equation. Green function gives us the evolution of temperature distribution with time. Such temperature distribution in space can be used to calculate average temperature rise, which is given by

\[
\overline{\theta(t)} = \frac{1}{x_2 - x_1} \int_{x_1}^{x_2} \theta(x,t) dx.
\]

Its expression is

\[
\overline{\theta(t)} = \frac{8 \dot{Q} l^3}{(l-x_1)k} \sum_{m=1}^{\infty} \frac{(1-e^{-m^2 \pi^2 at/4l^2})}{m^4 \pi^4} \left(\frac{(-1)^m}{2} \cos \frac{m\pi x_1}{2l} \right)^2.
\]

The solution of heat conduction with a modulated laser as a heating source is constructed from \(\overline{\theta(t)}\). For a modulated laser with modulation frequency \(f_0\), its laser-on time \(t_0\) is equal to \(1/(2f_0)\). The heating effect of the first laser pulse is given by \(\overline{\theta(t)}_{\text{pulse}} = \overline{\theta(t)}\) (\(0 < t < t_0\)). In the following laser-absent time, temperature decreases due...
to the absence of an energy source. The resulting temperature variation in this period can be regarded as the superposition of heating effect from a positive energy source $+\dot{Q}$ and a negative energy source $-\dot{Q}$. The positive heating effect is $\tilde{\theta}(t)$, and the negative heating effect is $-\tilde{\theta}(t+t_0)$. Therefore, temperature variation in the laser-absent period is $\tilde{\theta}(t)_{\text{pulse}} = \tilde{\theta}(t) - \tilde{\theta}(t+t_0)$. Similarly, temperature variation in the second pulse duration is $\tilde{\theta}(t)_{\text{pulse}} = \tilde{\theta}(t) - \tilde{\theta}(t+t_0) + \tilde{\theta}(t+2t_0)$. Thus, the final steady temperature variation during laser-on time can be generalized as

$$\tilde{\theta}(t)_{\text{pulse}} = \tilde{\theta}(t) + \sum_{n=1}^{\infty} (-1)^n \tilde{\theta}(t+nt_0).$$  

(6.3)

This equation suggests that the modulated square-wave laser heating solution is the alternative addition and subtraction of the step-wave laser heating solution. It can be further converted into the following form ($0 < t < t_0$)

$$\tilde{\theta}(t)_{\text{pulse}} = \frac{8\dot{Q}l^3}{(l-x_1)k} \sum_{m=1}^{\infty} \frac{1}{m^4 \pi^4} \left[ \frac{1-e^{-m^2\pi^2at/4l^2}}{1+e^{-m^2\pi^2at/(8f^2l^2)}} \right] \left\{ 1 - (-1)^m \cos \frac{m\pi x_1}{2l} \right\}^2. \quad (6.4)

The maximum spatially averaged temperature rise $\dot{\theta}_{\text{pulse, max}}$ can be determined from equation (6.4) when $f_0$ approaches 0. $\dot{\theta}_{\text{pulse, max}}$ is used as the reference to normalize $\tilde{\theta}(t)_{\text{pulse}}$. The normalized spatially averaged temperature rise $\tilde{\theta}(t)_{\text{pulse, nor}}$ is given by

$$\tilde{\theta}(t)_{\text{pulse, nor}} = \frac{\sum_{m=1}^{\infty} \frac{1}{m^4 \pi^4} \left[ \frac{1-e^{-m^2\pi^2at/4l^2}}{1+e^{-m^2\pi^2at/(8f^2l^2)}} \right] \left\{ 1 - (-1)^m \cos \frac{m\pi x_1}{2l} \right\}^2}{\sum_{m=1}^{\infty} \frac{1}{m^4 \pi^4} \left\{ 1 - (-1)^m \cos \frac{m\pi x_1}{2l} \right\}^2}. \quad (6.5)
6.4 Method of Constructing Theoretical Raman Spectrum

The instantaneous Raman signal \( I(\omega) \) during laser-one time has Gaussian distribution as

\[
I(\omega) = A_t \exp \left[ -\frac{4 \ln 2 \cdot (\omega - \omega_t)^2}{\Gamma_t^2} \right]. \tag{6.6}
\]

\( A_t \) is intensity at wavenumber \( \omega_t \), and \( \Gamma_t \) is linewidth. In a moderate temperature range, \( A_t, \omega_t \) and \( \Gamma_t \) are a linear function of the normalized average temperature rise \( \bar{\theta}(t)_{\text{pulse, nor}} \). \( A_t = A_0 (1 - \bar{A} \theta_{\text{pulse, nor}}) \), \( \omega_t = \omega_0 - B \bar{\theta}_{\text{pulse, nor}} \), and \( \Gamma_t = \Gamma_0 + C \bar{\theta}_{\text{pulse, nor}} \). \( A_0, \omega_0 \) and \( \Gamma_0 \) are intensity, wavenumber and linewidth obtained from the intrinsic Raman spectrum of the c-Si cantilever excited with a low-power laser beam at room temperature. \( A_0 \) is the multiple relating the theoretical normalized intensity \( (1 - \bar{A} \theta_{\text{pulse, nor}}) \) to experimental data. \( A, B \) and \( C \) give the total variation of normalized intensity, wavenumber and linewidth at the “steady state”. To obtain overall Raman spectrum, which is an accumulation of Raman scattering during the entire laser-on period \( t_0[1/(2f_0)] \), \( I(\omega) \) is integrated over the laser-on time \( t_0 \)

\[
I(\omega, t_0) = A_0 \int_{0}^{t_0[1/(2f_0)]} (1 - \bar{A} \theta_{\text{pulse, nor}}) \cdot \exp(-\frac{4 \ln 2 \cdot [x - (\omega_0 - B \bar{\theta}_{\text{pulse, nor}})]^2}{(\Gamma_0 + C \bar{\theta}_{\text{pulse, nor}})^2}) \, dt. \tag{6.7}
\]

To simplify analysis, accumulated Raman scattering are averaged by the laser-on time as

\[
\bar{I}(\omega, f_0) = \frac{A_0}{1/(2f_0)} \int_{0}^{t_0[1/(2f_0)]} (1 - \bar{A} \theta_{\text{pulse, nor}}) \cdot \exp(-\frac{4 \ln 2 \cdot [x - (\omega_0 - B \bar{\theta}_{\text{pulse, nor}})]^2}{(\Gamma_0 + C \bar{\theta}_{\text{pulse, nor}})^2}) \, dt. \tag{6.8}
\]

By substituting \( \bar{\theta}_{\text{pulse, nor}} \) with the equation (6.5), the full expression of \( \bar{I}(\omega, f_0) \) can be obtained. Based on this equation, theoretical Raman spectra at different modulation frequency can be calculated. By fitting experimental data with the theoretical
variation of intensity, wavenumber, and linewidth against modulation frequency, the only unknown parameter, thermal diffusivity $\alpha$, can be determined. The large noise of linewidth makes the determination of thermal diffusivity inaccurate. Consequently, only intensity and wavenumber are used to determine thermal diffusivity $\alpha$.

### 6.5 Determination of Thermal Diffusivity from Wavenumber and Intensity

In the fitting process, initial values of $A$, $B$, $C$ are obtained from experimental data directly as $A=2(I_{qs}-I_s)/(2I_{qs}-I_s)=0.3293$, $B=2(\omega_{qs}-\omega_s)=3.2 \text{ cm}^{-1}$, $C=2(\Gamma_s-\Gamma_{qs})=1.16 \text{ cm}^{-1}$. $I_{qs}$, $\omega_{qs}$, and $\Gamma_{qs}$ are intensity, wavenumber and linewidth of Raman spectrum obtained from the “quasi-steady state”. $I_s$, $\omega_s$, and $\Gamma_s$ are intensity, wavenumber and linewidth of Raman spectrum obtained from the “steady state”. In addition, we know $\omega_0=\omega_s+B$ and $\omega_0=520.78 \text{ cm}^{-1}$. Moreover, $\Gamma_0 = \Gamma_s - C$ and $\Gamma_0 = 10.42 \text{ cm}^{-1}$. However, as our lower and upper limit frequency are not sufficiently low and high, $A$, $B$, $C$, $\omega_0$ and $\Gamma_0$ deviate from their real values a little bit. As a result, values of these parameters should be refined within a small range. Theoretically, modulation frequency can be further increased to achieve a converged state, which can improve the accuracy of $A$, $B$, $C$, $\omega_0$ and $\Gamma_0$. However, at a high modulation frequency, heat conduction in the c-Si cantilever will have prominent two-dimensional effect due to the ~$\mu$m-thick volumetric laser absorption at the cantilever surface.

In theory, $A$, $B$, $C$, $\omega_0$ and $\Gamma_0$ should be refined to approach their real values in a fitting process. However, in practice, not all of these parameters are refined. $C$ and $\Gamma_0$ are not refined because they have a low sensitivity to temperature. As parameters related to wavenumber, $B$ and $\omega_0$ are independent from each other. In a fitting process, for each $B$,
one best $\omega_0$ can be quickly identified to minimize the difference between fitting and experimental data. Similarly, $A_0$ and $A$ are independent from each other: $A_0$ determines the absolute value of intensity, and $A$ gives the relative change. $A_0$ can be determined easily from the best fitting curve to experimental data. As a result, only the refinement of $A$ and $B$ are required in a fitting process. The sensitivity of $A$ and $B$ for achieving the best fitting are different to wavenumber and intensity. $A$ takes the major role for achieving the best fitting to intensity, while $B$ takes the major role for achieving the best fitting to wavenumber. Thermal diffusivity $\alpha$, which determines how fast/slow intensity and wavenumber can change with $f$, is scanned from $1.01 \times 10^{-5}$ m$^2$/s to $18 \times 10^{-5}$ m$^2$/s with an increment of 1%. The discrepancy of a fitting curve to experimental data is evaluated with least square method.

The refined $A$ and $B$ obtained from experimental data of intensity are denoted as $A_{int}$ and $B_{int}$. The refined $A$ and $B$ obtained from experimental data of wavenumber are denoted as $A_{fre}$ and $B_{fre}$. In theory, $A_{int}$ is equal to $A_{fre}$, and $B_{int}$ is equal to $B_{fre}$. However, in an actual case, this is impossible due to experimental errors. Since $A$ is sensitive to intensity and $B$ is sensitive to wavenumber, $A_{int}$ and $B_{fre}$ are used to extract thermal diffusivity $\alpha$. $A_{int}$ is determined as 0.33, and $B_{fre}$ is determined as 3.3. The best fitting curve to experimental data of intensity is plotted with a red line in Fig. 6.4 (a). Its thermal diffusivity $\alpha$ is $9.57 \times 10^{-5}$ m$^2$/s. To show the 10% uncertainty of thermal diffusivity $\alpha$, the blue curve with thermal diffusivity of $8.61 \times 10^{-5}$ m$^2$/s and the green one with thermal diffusivity of $10.53 \times 10^{-5}$ m$^2$/s are plotted in Fig. 6.4 (a). Similarly, the best fitting curve to experimental data of wavenumber is also plotted with a red line in Fig. 6.4 (b). Its thermal diffusivity $\alpha$ is $11.00 \times 10^{-5}$ m$^2$/s. Also, the blue curve with thermal diffusivity of
9.90×10⁻⁵ m²/s and the green one with thermal diffusivity of 12.00×10⁻⁵ m²/s are plotted to display the 10% uncertainty of thermal diffusivity. Obviously, in both cases, the blue curve and the green curve can be distinguished from the best fitting curve easily.

Figure 6.4 (a) The variation of intensity against modulation frequency. The best fitting curve with thermal diffusivity α of 9.57×10⁻⁵ m²/s is plotted by a red line. Thermal diffusivity of the blue curve and the green curve are 8.61×10⁻⁵ m²/s and 10.53×10⁻⁵ m²/s. (b) The variation of wavenumber against modulation frequency. The best fitting curve with thermal diffusivity of 11.00×10⁻⁵ m²/s is plotted by a red line. Thermal diffusivity of the blue curve and the green curve are 9.90×10⁻⁵ m²/s and 12.00×10⁻⁵ m²/s.

6.6 Determination of Thermal Diffusivity from Total Raman Emission

Total Raman peak area is another parameter can be employed to probe local temperature rise. In fact, it reflects the total Raman emission over the whole peak range of wavenumber. At any instant, Raman emission is a function of temperature. The total Raman emission is the integral of transient Raman emission during the laser-on time 1/(2f₀), which is given by

$$E_{total} = A_c \int_0^{1/(2f_0)} (1 - A_c \bar{\theta}_{mw}) dt.$$  (6.9)

Since experimental data is the time-averaged total Raman emission, the total Raman emission calculated above is averaged by 1/(2f₀) with the following equation
\[ E = \frac{A_e'}{1/(2f_0)} \int_0^{1/(2f_0)} (1 - A_e \bar{\theta}_{nor}) dt, \]

(6.10)

where \( A_e \) gives the total variation of the normalized total Raman emission from the “steady state” to the “room-temperature state”. \( A_e' \) is a multiple relating the normalized theoretical data to experimental data. When this function is employed to fit experimental data, the fitting result is determined by \( A_e \) and \( \alpha \).

Figure 6.5 The variation of total Raman emission against modulation frequency. The best fitting curve with thermal diffusivity of \( 9.02 \times 10^{-5} \text{ m}^2/\text{s} \) is plotted by a red line. Thermal diffusivity of the blue curve and the green curve are \( 8.11 \times 10^{-5} \text{ m}^2/\text{s} \) and \( 9.00 \times 10^{-5} \text{ m}^2/\text{s} \). The blue curve and the green curve display the 10% uncertainty of thermal diffusivity.

The fitting process of total Raman emission is same to that of intensity and wavenumber. \( A_e \) is scanned from \( 5 \times 10^{-3} \) to 1 with an increment of \( 5 \times 10^{-3} \), and \( \alpha \) is scanned from \( 10^{-5} \text{ m}^2/\text{s} \) to \( 18 \times 10^{-5} \text{ m}^2/\text{s} \) with an increment of 1%. The best fitting curve to experimental data is given by a red line when \( A_e \) is equal to 0.295 and \( \alpha \) is equal to \( 9.02 \times 10^{-5} \text{ m}^2/\text{s} \), as shown in Fig. 6.5. \( A_e \) is a little smaller than \( A \) because linewidth broadens with increased temperature. The blue and green curves in Fig. 6.5 are plotted to represent a 10% deviation from the best-fitted thermal diffusivity. Thermal diffusivity of the blue curve is \( 9.02 \times 10^{-5} \text{ m}^2/\text{s} \), and thermal diffusivity of the green curve is \( 9.57 \times 10^{-5} \).
Total Raman emission provides an easy and convenient way to determine thermal diffusivity with a relatively high accuracy. It avoids the time-consuming process of extracting intensity, wavenumber and linewidth from reconstructed theoretical Raman spectrum.

6.7 Physical Analysis and Experimental Uncertainty Evaluation

To evaluate the measurement accuracy of FR-Raman, thermal diffusivity is estimated from our physical model. This is done by estimating temperature rise of the whole c-Si cantilever, and then finding the reference value of thermal diffusivity at our estimated temperature rise. At the “steady state”, the c-Si cantilever tip has a maximum average temperature rise $\theta_s$. $\theta_s$ can be calculated by $q=ka\theta_s/L$. $q$ is the absorbed laser power which is the product of the incident laser power and the absorbance of c-Si (0.626 at 532 nm). $k$ is thermal conductivity of c-Si, which is equal to 148 W/m·K at 300K. $A$ is the cross-section area of the c-Si cantilever. Thus, $\theta_s$ is equal to 56.98 K. At the “quasi-steady state”, the average temperature rise of the c-Si cantilever tip is 28.49 K since $\theta_{qs}$ is equal to $\theta_s/2$. Thus, the average temperature rise of the c-Si cantilever tip is between 28.49 to 56.98 K. From the c-Si cantilever tip to the Si chip, temperature rise linearly decreases to 0 K. Therefore, the spatially average temperature rise of the whole Si cantilever $\theta_{avg}$ is between 14.25 and 28.49 K. Since the experiment is conducted at room temperature (293 K), the absolute average temperature of the whole Si cantilever is between 307.25 and 321.49 K. The reference value of thermal diffusivity of c-Si is $8.66 \times 10^{-5}$ m$^2$/s at 307.25 K and $8.16 \times 10^{-5}$ m$^2$/s at 321.49 K. Therefore, thermal diffusivity of the whole c-Si cantilever should be between $8.16 \times 10^{-5}$ and $8.66 \times 10^{-5}$ m$^2$/s.
Thermal diffusivity determined from intensity, wavenumber and total Raman emission is 9.57×10⁻⁵, 11.00×10⁻⁵, and 9.02×10⁻⁵ m²/s, respectively. These values are a little larger than the upper limit of estimated thermal diffusivity. Such deviation is related to the influence of thermal stress on Raman spectrum. Due to the existence of temperature gradient along the c-Si cantilever, thermal stress can be induced in the c-Si cantilever, which can further result in some degree of cantilever deflection. This can result in decreased intensity, redshift wavenumber and broadening linewidth. Such variation is same to the variation of Raman spectrum when temperature increases. In fact, the variation of Raman spectrum obtained in this experiment is a result of both temperature and thermal stress. Therefore, Raman spectrum have larger and faster change in intensity, wavenumber and total Raman emission against modulation frequency. This leads to a larger thermal diffusivity. The thermal-stress effect can be mediated by using a higher sensitivity spectrometer, which can obtain strong Raman spectrum even the laser power is small. The influence of thermal radiation and convection on thermal diffusivity can be estimated as \((8\varepsilon\sigma T_0^3 + 4h)L^2 / (\rho c_p \delta T^2)\). ⁵⁷,⁵⁸ \(\varepsilon\) is the emissivity of c-Si at 300 K (<0.1). \(h\) is the free convection coefficient, which is about 1–2 W/m²·K at 300K. The thermal radiation and convection effect give a negligible error of \(~4.8\times10^{-8}\) m²/s in thermal diffusivity.
CHAPTER 7. CHARACTERIZATION OF ANISOTROPIC THERMAL CONDUCTIVITY OF SUSPENDED NM-THICK BLACK PHOSPHORUS WITH FREQUENCY-RESOLVED RAMAN SPECTROSCOPY

Previous chapter introduces FR-Raman by measuring thermal diffusivity of a c-Si cantilever. In this chapter, we further develop this technique and apply it to measure the anisotropic in-plane thermal conductivity of BP. Four BP samples with thickness between 99.8 and 157.6 nm are studied. Our results show the armchair thermal conductivity is 13.5~22 W m\(^{-1}\) K\(^{-1}\), and the zigzag thermal conductivity is 39.8~62.7 W m\(^{-1}\) K\(^{-1}\). These results are in good agreement with literature reports.

7.1 Physical Principles of Measurement

The in-plane thermal conductivity of BP is measured when a BP sample is suspended on a square dent (22×22×3 μm\(^3\)), which is fabricated on Si wafer with focused ion beam (FIB). As shown in Fig. 7.1 (a), the armchair or zigzag direction is deliberately aligned along an edge of the square dent. In practice, this is achieved by aligning a nature-formed edge of an exfoliated BP sample along one arbitrary edge of a square dent. Previous research has adequately confirmed that a BP’s nature-formed edge is always in the armchair or zigzag direction.\(^{47,59}\) Note that we only choose a BP sample with at least one nature-formed edge to prepare a suspended BP sample. However, from the natural-formed edge of a BP sample, we cannot distinguish between the armchair direction and the zigzag direction. Therefore, OT-Raman is used to identify the crystalline orientation. This step can tell us which direction, armchair or zigzag, is along the nature-formed edge of a BP sample.
Figure 7.1  (a) Schematic of a BP sample suspended on a square dent (22×22×3 μm$^3$). The armchair/zigzag direction is along edges of the square dent. (b) The irradiation of a “as transferred” suspended BP sample by a modulated laser beam. (c) The irradiation of a “as transferred” suspended BP sample by a CW laser beam. (d) The irradiation of a “laser modified” suspended BP sample by a CW laser beam.

In a FR-Raman experiment, first, we irradiate the “as transferred” sample with a modulated laser beam and measure its Raman spectra over a wide modulation frequency range [Fig. 7.1 (b)]. The variation of wavenumber against modulation frequency can be obtained from this measurement. Then, the “as transferred” sample [Fig. 7.1 (c)] is irradiated with a CW laser. Raman spectra excited with various laser powers are acquired, from which the wavenumber-power differential $\Phi_1$ can be obtained. Note that $\Phi_1$ depends on the armchair thermal conductivity $\kappa_{AC}$ and the zigzag thermal conductivity $\kappa_{ZZ}$. Then we cut two sample’s edges along the armchair direction (Fig. 7.1d) to separate it from Si substrate. This is achieved by using a high-power CW laser beam. The “laser modified” sample is irradiated with a CW laser of varying power, from which its $\Phi_2$ can
be obtained. The “laser modified” sample enables the isolation of heat conduction along the armchair direction. Therefore, for this sample, Φ₂ is predominantly determined by \( \kappa_{AC} \). The thermal conductivity ratio \( \eta \) \( (\kappa_{ZZ}/\kappa_{AC}) \) can be determined from \( \Phi_2/\Phi_1 \). The absolute value of \( \kappa_{AC} \) and \( \kappa_{ZZ} \) are extracted from the normalized average temperature rise \( \theta_{nor} \), which is converted from wavenumber. We emphasize that, to keep the consistency of FR-Raman experiments conducted on various BP samples, laser polarization is always aligned along the armchair direction.

### 7.2 Experimental Procedures and Data Processing Method

We take measurements performed on the 157.6-nm thick BP sample as an example to demonstrate experimental procedures and data processing methods. Figure 7.2 (a) and (b) show optical images of the “as transferred” 157.6-nm thick sample and its “laser modified” counterpart. The uniform color of the suspended area suggests it has a uniform thickness. The “as transferred” sample has a 22×22 \( \mu \text{m}^2 \) suspended area, and the “laser modified” one has a 18.12×22 \( \mu \text{m}^2 \) suspended area. The sample thickness is determined directly from the supported area, which is closely adjacent to the suspended area. Figure 7.2 (c) shows the AFM image of the area within yellow dashed lines [Figure 7.2 (b)]. The height profile along the white line in the AFM image shows that the BP sample is 157.6-nm thick [Figure 7.2 (d)]. The FR-Raman experiment involves measurements of two series of data: the variation of wavenumber with modulation frequency \( \omega(f) \); the variation of wavenumber with CW laser power \( \omega(P) \). The following section describes how these data are measured.
Figure 7.2 (a) Optical image of the “as transferred” 157.6-nm thick sample. The armchair/zigzag direction is perpendicular/parallel to the nature-formed edge of the BP sample. The suspended area of the BP sample is $22 \times 22$ μm$^2$. The red dot marks the center of the suspended area, which is irradiated by a focused laser beam for thermal characterization. (b) Optical image of the “laser modified” 157.6-nm thick sample. Its suspended area is $18.12$ μm $\times 22$ μm. The red dot marks the center of the suspended area, which is irradiated by a focused laser beam for thermal characterization. The area within yellow dashed lines is thoroughly characterized by AFM. (c) AFM image of the BP area within yellow dashed lines. The thickness of the BP sample is determined from the height profile along the white line. (d) Height profile along the white line in the AFM image. The thickness is determined as 157.6 nm.

7.2.1 Measurement of $\omega(f)$

In the FR-Raman experiment, an electro-optics modulation (EOM), which is driven by a function generation, is introduced into the optical path of the Raman system (described in Chapter 2). EOM can modulate a CW laser with a square waveform at a frequency as high as 20 MHz. For the 157.6-nm thick sample, it is irradiated by a square-wave modulated laser at frequencies in a range of 1000 Hz to 20 MHz. This modulation frequency range is broad enough to induce thermal response from the “quasi-steady state”
to the “steady state”. We take great care on selecting an appropriate laser power, so that the sample will not be damaged while sufficiently strong Raman signals can be excited. Here, we use $P_m$ to represent the power of a modulated laser during the laser-on time. Once an appropriate $P_m$ is selected, it is kept constant regardless of modulation frequency. These acquired Raman spectra are shown by a contour map in Fig. 7.3 (a). The most notable features of these Raman spectra are three Raman peaks $A_g^1$, $B_{2g}$, and $A_g^2$ at 361, 438 and 466 cm$^{-1}$, respectively. $^{60,61}$ They demonstrate strong variation in wavenumber against $f$, but very weak variation in intensity and linewidth. The $A_g^2$ peak wavenumber ($\omega$) is used to monitor local temperature rise and extract the anisotropic thermal conductivity of BP due to its high thermal sensitivity. The $A_g^2$ peak wavenumber ($\omega$) is plotted against modulation frequency $f$ in Fig. 7.3 (b). As we have expected, $\omega$ increases with increased $f$, and it has a total variation of $\sim 1.0$ cm$^{-1}$ (from $\sim 464$ to $\sim 465$ cm$^{-1}$). The convergence of $\omega(f)$ at the high and low $f$ is the solid evidence that the transition from the “quasi-steady state” to the “steady state” does happen. $\omega(f)$ is dependent on BP’s thermal properties and the absorbed laser power. BP’s thermal properties determine how fast $\omega$ can vary from the “quasi-steady state” to the “steady state”. The absorbed laser power determines how large $\omega$ can change from the “quasi-steady state” to the “steady state”. To eliminate the influence of the absorbed laser power, we need to convert $\omega(f)$ into the normalized average temperature rise $\overline{\theta}_{nor}$. This conversion is accomplished by using data obtained from the variation of wavenumber with CW laser power $\omega(P)$. 
Figure 7.3  (a) Raman spectra of the “as transferred” 157.6-nm thick sample excited by a modulated laser with frequencies from 1000 Hz to 20 MHz. Color of the contour gives the intensity of Raman spectrum at a specific wavenumber. (b) The variation of the $A_g^2$ mode wavenumber $\omega$ with modulation frequency $f$. The total variation is $\sim 1.0$ cm$^{-1}$. (c) Raman spectra of the “as transferred” 157.6-nm thick sample (c-1) and the “laser modified” 157.6-nm thick sample (c-2) excited by various laser powers. Color of the contour gives the intensity of Raman spectrum at a specific wavenumber. (d) The variation of the $A_g^2$ mode wavenumber with laser power. The red (blue) dots represent experimental data obtained from the “as transferred” (“as modified”) sample. The best fitting linear function to experimental data is given by a line.

7.2.2 Measurement of $\omega(P)$

Turning on/off EOM allows an easy and rapid switching between a modulated laser and a CW laser. This measurement is conducted when EOM is turned off and a CW
laser becomes the energy source. Various laser powers are applied to irradiate the “as transferred” sample. Here, we emphasize that, no matter what laser powers are used, the largest one $P_{\text{max}}$ must be equal to $P_m$. Considering its significant importance for the normalization, the thermal response to the CW laser with a power of $P_{\text{max}}$ is defined as the “CW steady state”. This thermal state is indeed equivalent to the “steady state” of the modulated laser with a power of $P_m$. At the “CW steady state”, wavenumber $\omega_s$ and the total variation in wavenumber $\Delta \omega$ are crucial to convert $\omega(f)$ into $\bar{\theta}_{\text{nor}}$. $\omega_s$ is directly obtained from experimental data, while $\Delta \omega$ is calculated from $\Phi_1 P_{\text{max}}$.

These Raman spectra excited by various laser powers are shown by the contour in Fig. 7.3 (c-1). Obviously, Raman spectra have increased intensity, redshifted wavenumber and broadening linewidth when laser power increases. The $A_g^2$ mode wavenumber is plotted against laser power with red dots in Fig. 7.3 (d). The wavenumber shows a linear dependence on laser power. The best fitting linear function to experimental data has $\Phi_1 = -0.528 \pm 0.009 \text{ cm}^{-1}/\text{mW}$. The above measurement is repeated on the “laser modified” sample with same series of laser powers. Its contour map also suggests that Raman spectra have increased intensity, redshifted wavenumber and broadening linewidth with increased laser power, as shown in Fig. 7.3 (c-2). Compared with the “as transferred” sample, the “laser modified” one has larger change in wavenumber. The $A_g^2$ mode wavenumber is plotted against laser power with blue dots in Fig. 7.3 (d). Experimental data are fitted by a linear function, which gives $\Phi_2 = -0.943 \pm 0.002 \text{ cm}^{-1}/\text{mW}$. In terms of the absolute value, $\Phi_2$ is much larger than $\Phi_1$. It suggests that the average temperature rise in the “laser modified” sample is much larger than that in the “as transferred” sample. This phenomenon results from the change in thermal transport
along the BP plane. For the “laser modified” sample, heat conduction to Si substrate happens only in the armchair direction. So, under the same power laser heating, it will have a higher temperature rise. Φ₁ and Φ₂ are essential to determine the anisotropy of the BP’s in-plane thermal conductivity.

### 7.3 Determination of the Anisotropic Thermal Conductivity

The complete characterization of the anisotropic thermal conductivity of BP requires the determination of two parameters: the thermal conductivity ratio η (κ_{ZZ}/κ_{AC}), and the armchair thermal conductivity κ_{AC}. This section introduces how to extract η and κ_{AC} from above experimental data.

#### 7.3.1 Determination of η

Φ₁ and Φ₂ are two key parameters to determine η. As we have mentioned before, Φ₁ and Φ₂ are measured from the “as transferred” sample and its “laser modified” counterpart. The “as transferred” sample has four edges closely attached to Si wafer. The Si wafer acts as a heat sink for dissipating laser-induced heat from the center of the suspended area. The heat sink temperature remains unchanged due to the high thermal conductivity of crystal silicon. Because the thermal conductivity of N₂ gas is negligible, laser-induced heat can only be dissipated along the BP plane. The interface thermal resistance between BP and Si has negligible effect on the heat transfer, so we believe that the temperature at the margin of the suspended BP area remains unchanged despite the middle of the suspended BP area is under the direct laser irradiation. In the “laser modified” sample, heat is forced to dissipate toward two paralleled edges along the armchair direction predominantly. In other words, the change in the configuration of a
suspended BP sample alters thermal transport in a way that heat dissipation in the zigzag direction is suppressed significantly. This leads to a higher temperature rise in the “laser modified” sample. For a simple description, under the irradiation of a unit incident laser power, the average temperature rise in the heating region of the “as transferred” sample and its “laser modified” counterpart are defined as $\Delta T_1$ and $\Delta T_2$, respectively. $\Phi_1 = \chi \cdot \Delta T_1$ and $\Phi_2 = \chi \cdot \Delta T_2$, where $\chi$ is the temperature coefficient. Hence, $\frac{\Phi_2}{\Phi_1}$ is equal to $\frac{\Delta T_2}{\Delta T_1}$. Despite $\Phi_2$ and $\Phi_1$ are dependent on $\kappa_{AC}$ and $\kappa_{ZZ}$, their ratio $\frac{\Phi_2}{\Phi_1}$ is only dependent on $\eta$. The variation of $\frac{\Delta T_2}{\Delta T_1}$ with $\eta$ can be simulated with the commercial software ANSYS. Then, by interpolating $\frac{\Phi_2}{\Phi_1}$ into the simulated curve of $\frac{\Delta T_2}{\Delta T_1}$, $\eta$ can be determined at last.

Due to the fact that a suspended BP sample has a lateral size much larger than its thickness, heat conduction in the thickness direction is negligible. Thus, we can model heat conduction in a suspended BP sample with the two-dimensional heat conduction equation

$$
\frac{\partial^2 T}{\partial x^2} + \eta \frac{\partial^2 T}{\partial y^2} = -\frac{\dot{Q}}{\kappa_{AC}},
$$

(7.1)

where $\dot{Q}$ is the volumetric optical absorption per unit time. The solving of the equation (7.1) gives the temperature rise $\Delta T$. $\Delta T$ is a function of three unknown parameters, $\eta$, $\kappa_{AC}$ and $\dot{Q}$. Since the equation (7.1) is a linear function, $\Delta T$ is proportional to $\left(\frac{\dot{Q}}{\kappa_{AC}}\right)$. This indicates that $\dot{Q}$ and $\kappa_{AC}$ can be eliminated in the expression of $\frac{\Delta T_2}{\Delta T_1}$. In other words, $\frac{\Delta T_2}{\Delta T_1}$ is just a function of $\eta$. 
Figure 7.4 Simulated normalized temperature rise distribution in the “as transferred” 157.6-nm thick sample (a) and “laser modified” 157.6-nm thick sample (b). White circles give the range of a heating source. (c) The theoretical curve of $\Delta T_2/\Delta T_1$ as a function of $\eta$. By interpolating $\Phi_2/\Phi_1=1.79$ into the theoretical curve, $\eta$ of the 157.6-nm thick sample is determined as 3.06.

We use the commercial software ANSYS to simulate $\Delta T_2$ and $\Delta T_1$ separately, and then calculate their ratio $\Delta T_2/\Delta T_1$. In ANSYS simulations, since $\Delta T_2/\Delta T_1$ is not relevant to $\dot{Q}$ and $\kappa_{AC}$, $\Delta T_2$ and $\Delta T_1$ can be calculated under arbitrary setting values of $\dot{Q}$ and $\kappa_{AC}$. For the “as transferred” sample, its boundaries are prescribed as constant temperature. For the “laser modified” one, boundaries along the zigzag direction are prescribed as constant temperature, while boundaries along the armchair direction are prescribed as insulated. Our numerical model strictly mimics the actual dimension of a sample. Figure 7.4 (a) and (b) show simulation results of the 157.6-nm thick sample when $\eta$ is set as 3. The simulated temperature rise distribution has been normalized. They have a same heating source, which is located within a white circle. The heating source has a radius equal to the $1/e^2$ radius of the focused laser beam, which is equal to 2 $\mu$m. As shown in Fig. 7.4 (a), there is radial heat flow from the heating source to borders. The shape of the heat front propagating through the BP plane is elongated in the zigzag direction due to its higher thermal conductivity. However, the normalized temperature rise distribution is
changed significantly in the “laser modified” sample. Due to the restricted heat conduction in the zigzag direction, heat flows with a plane wavefront in two opposite directions toward borders. Compared with the normalized temperature rise distribution in Fig. 7.4 (a), the heating source has a much stronger heating effect. Also, the normalized temperature rise distribution extends to a much larger area outside the heating source. This phenomenon can probably result in the measurement error of $\eta$, which will be discussed in detail in the following section. In these two cases of simulations, their normalized average temperature rise within white circles are $\Delta T_1$ and $\Delta T_2$, respectively. By repeating simulations with different setting values of $\eta$, we eventually have the theoretical curve of $\Delta T_2/\Delta T_1$, as shown in Fig. 7.4 (c). For the 157.6-nm thick sample, $\Phi_2/\Phi_1$ is measured at 1.79. Then, $\eta$ is determined as 3.06 by interpolation. With known $\eta$, we can continue to calculate $\kappa_{AC}$ from $\omega(f)$.

### 7.3.2 Determination of $\kappa_{AC}$

The determination of $\kappa_{AC}$ requires comparisons between the experimental normalized average temperature rise $\bar{\theta}_{nor,e}$ and its simulated counterpart $\bar{\theta}_{nor,s}$. Treated as a free parameter, $\kappa_{AC}$ is determined by adjusting its value until the standard deviation between $\bar{\theta}_{nor,e}$ and $\bar{\theta}_{nor,s}$ is minimized. $\bar{\theta}_{nor,e}$ is calculated from $\omega(f)$ using the following expression

$$\bar{\theta}_{nor,e} = 1 + (\omega(f) - \omega_s)/\Delta\omega,$$

(7.2)

where $\Delta\omega$ and $\omega_s$ are parameters obtained from the “CW steady state”. In theory, $\bar{\theta}_{nor,e}$ decreases from 1 (the “steady state”) to 0.5 (the “quasi-steady state”) with increased $f$. However, in actual cases, measurement errors of $\Delta\omega$ and $\omega_s$ lead to the deviation of
\( \bar{\theta}_{\text{nor,e}} \) more or less. Here, we use a factor \( C \) to correct \( \bar{\theta}_{\text{nor,e}} \). The corrected \( \bar{\theta}_{\text{nor,e}} \) has an expression of

\[
\bar{\theta}_{\text{nor,e}} = 1 + C \cdot \left[ \omega(f) - \omega_0 \right] / \Delta \omega.
\]  

(7.3)

After the correction with parameter \( C \), \( \bar{\theta}_{\text{nor,e}} \) is guaranteed to vary from 1 to 0.5 with increased \( f \). The correction leads to an improved fitting result. The measurement error induced by the correction will be discussed in the next section. For the 157.6-nm thick sample, its \( \bar{\theta}_{\text{nor,e}} \) after the correction is plotted with black dots in Fig. 7.5 (a). These experimental data are the average of 10 measurements. Their error bars are the standard deviation of 10 measurements. At high frequencies, experimental data have relatively larger standard deviation, which is relevant to the deformation of the modulated laser waveform.

The calculation of \( \bar{\theta}_{\text{nor,s}} \) requires simulations of thermal response to a modulated laser. However, such simulations are complicated and time-consuming even with the help of ANSYS. Therefore, a semi-analytical method is developed to simplify and expedite simulations. This method takes advantage of ANSYS to simulate the thermal response to a step-laser first. Then, based on the temperature linear response and the superposition law, the thermal response to a modulated laser can be constructed from the thermal response to a step-wave laser. Modeled with the two-dimensional thermal transport in ANSYS, the thermal response to a step-laser is represented with \( \theta_s(t) \). \( \theta_s(t) \) represents temperature rise as a function of time. Therefore, the thermal response to a modulated laser with a frequency \( f \) is given by

\[
\theta_m(t_p) = \sum_{n=0}^{\infty} (-1)^n \cdot \theta_s(t_p + n \cdot \tau_h),
\]  

(7.4)
where $t_h$ (laser-on time) is equal to $1/(2f)$. $\theta_m(t_p)$ gives the evolution of the temperature rise at a steady periodic thermal state during $t_h$. Its corresponding average temperature rise during $t_h$ is

$$\overline{\theta}_m = \frac{\int_0^{t_h} \theta_m(t_p) dt}{t_h}. \tag{7.5}$$

When $t_h$ is infinitely large, we have $\overline{\theta}_\infty$, which is the average temperature rise at the “steady state”. Normalize $\overline{\theta}_m$ with $\overline{\theta}_\infty$, we have the simulated normalized average temperature rise $\overline{\theta}_{nor\_s}$ which is equal to

$$\overline{\theta}_{nor\_s} = \frac{\int_0^{t_h} \theta_m(t_p) dt}{t_h \cdot \overline{\theta}_\infty}. \tag{7.6}$$

$\overline{\theta}_{nor\_s}$ is a function of $f$ and $\kappa_{AC}$. The variation of $\overline{\theta}_{nor\_s}$ with $f$ is only determined by $\kappa_{AC}$ since we already know $\eta$. By calculating the variation of $\overline{\theta}_{nor\_s}$ with $f$ at various trial values of $\kappa_{AC}$, we can obtain theoretical curves for fitting experimental data.

Three theoretical curves of the 157.6-nm thick sample are plotted in Fig. 7.5 (a). The red one is the best fitting curve to $\overline{\theta}_{nor\_s}$ with $\kappa_{AC}$ equal to 20.5 W m$^{-1}$ K$^{-1}$. The green and blue curves are calculated when $\kappa_{AC}$ is equal to 16 and 26 W m$^{-1}$ K$^{-1}$, respectively. The best fitting curve has the smallest standard deviation $\delta$, which is identified from the parabolic-like $\kappa_{AC}$–$\delta$ curve in Fig. 7.5 (b). The smallest $\delta$ has been marked with a red dot in Fig. 7.5 (b).
Figure 7.5 (a) The fitting of experimental data by various theoretical curves. Experimental data are plotted with black dots. Their error bars represent the standard deviation. The best fitting curve to experimental data is plotted with red color. Its $\kappa_{AC}$ is equal to 20.5 W m$^{-1}$ K$^{-1}$. The green and blue curves are calculated with $\kappa_{AC}$=16 and $\kappa_{AC}$=26 W m$^{-1}$ K$^{-1}$, respectively. (b) The standard deviation $\delta$ of experimental data to theoretical curves as a function of $\kappa_{AC}$. The red dot shows the smallest $\delta$. Its corresponding $\kappa_{AC}$ is 20.5 W m$^{-1}$ K$^{-1}$.

7.4 Measurement Results and Discussion

In total, four samples with thickness of 99.8, 112.3, 145.9 and 157.6 nm are successfully prepared and studied. Measurement results are listed in Table 1. It can be found that $\kappa_{AC} = 13.5$-22 and $\kappa_{ZZ} = 39.8$-62.7 W m$^{-1}$ K$^{-1}$. They are comparable to these results obtained by micro-Raman spectroscopy ($\kappa_{AC} = \sim 20$ and $\kappa_{ZZ} = \sim 40$ W m$^{-1}$ K$^{-1}$) $^{10}$, TDTR technique ($\kappa_{AC} = 26$-34 and $\kappa_{ZZ} = 62$-86 W m$^{-1}$ K$^{-1}$ by Jang et al., and $\kappa_{AC} = 23$-33 and $\kappa_{ZZ} = 73$-93 W m$^{-1}$ K$^{-1}$ by Sun et al.) $^{17,19}$, and micro-bridge technique ($\kappa_{AC}$ decreases from $\sim 15$ to $\sim 5$ W m$^{-1}$ K$^{-1}$, and $\kappa_{ZZ}$ decreases from $\sim 27$ to $\sim 12$ W m$^{-1}$ K$^{-1}$ as thickness varies from $\sim 300$ to $\sim 50$ nm) $^{20}$. The discrepancy of these experimental measurements is relevant to their methods for sample preparation, data processing and thermal transport modeling. Our measured results have demonstrated large measurement errors. Two common effects, thickness effect and oxidation effect, are not responsible to the large data deviation in our work. Previous research has concluded that the in-plane thermal
conductivity increases with increased thickness in BP due to the strong surface scattering. Thickness effect is excluded by our observed irregular dependence of $\kappa_{AC}$ and $\kappa_{ZZ}$ on the thickness. Meanwhile, oxidation effect is negligible since our BP samples are protected well by dry N$_2$ gas. $^{42,44}$ So far, we believe measurement errors originate from factors, such as the gravity-induced deformation, the existence of micro-wrinkles/micro-bubbles, the temperature dependence of BP’s physical properties, and the correction of normalized data. Here, we study measurement errors by analyzing $\eta$ and $\kappa_{AC}$, which are two independent parameters ($\kappa_{ZZ}$ is calculated by $\kappa_{ZZ} = \eta \cdot \kappa_{AC}$).

### Table 1
Experimental results of 99.8, 112.3, 145.9 and 157.6-nm thick suspended BP samples. $\eta$ and $\kappa_{AC}$ are extracted from experimental data. $\kappa_{ZZ}$ is calculated from $\eta$ and $\kappa_{AC}$.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>$\eta$</th>
<th>$\kappa_{AC}$ (W m$^{-1}$ K$^{-1}$)</th>
<th>$\kappa_{ZZ}$ (W m$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.8</td>
<td>2.64</td>
<td>21</td>
<td>55.4</td>
</tr>
<tr>
<td>112.3</td>
<td>1.86</td>
<td>22</td>
<td>40.9</td>
</tr>
<tr>
<td>145.9</td>
<td>2.95</td>
<td>13.5</td>
<td>39.8</td>
</tr>
<tr>
<td>157.6</td>
<td>3.06</td>
<td>20.5</td>
<td>62.7</td>
</tr>
</tbody>
</table>

In the ANSYS simulation model, we assume that the supported area of BP contacts perfectly with Si substrate and the suspended area of BP is completely flat. However, these assumptions are challenged by facts that micro-wrinkles/micro-bubbles exist between the supported area of BP and Si substrate, and the suspended area of BP is deformed under the force of gravity. $^{21,65-67}$ The existence of micro-wrinkles/micro-bubbles makes it inaccurate to describe the boundaries of suspended area with constant temperature in the thermal transport model. With a large suspended area, the gravity-induced deformation is inevitable. For a “as transferred” sample and its “laser modified”
counterpart, their suspended area is at different states of force balance. Typically, the suspended area of a “laser modified” sample has larger deformation than that of a “as transferred” sample. The deformation has two effects: the area under the direct irradiation of a laser beam is larger than the laser spot size; and the actual suspended area is relatively larger than it should be. The micro-wrinkles/micro-bubbles and deformation are morphological features closely related to characteristic of each sample. As a result, measurement errors of $\eta$ and $\kappa_{AC}$ are related to sample characteristics.

The temperature dependence of BP’s physical properties also contributes to large measurement errors of $\eta$. As shown in Fig. 7.4 (a) and (b), compared with the “as transferred” sample, the “laser modified” one has a higher normalized temperature rise and a larger normalized temperature rise distribution. Physical properties of these two samples are under the influence of temperature. Apparently, physical properties of the “laser modified” sample are under a larger influence of temperature. However, in ANSYS simulations, we do not consider the temperature dependence of BP’s physical properties, and simply use their values at 300 K to conduct numerical calculations. Such mismatch in the model and actual conditions leads to measurement errors of $\eta$. The degree of the influence of the mismatch on the determination of $\eta$ is sample-dependent, since appropriate laser powers applied to conduct an experiment are sample-dependent. Combined with the deformation and micro-wrinkles/micro-bubbles, they together lead to large measurement errors of $\eta$.

The correction of normalized data $\tilde{\theta}_{nor,e}$ plays another important role on measurement errors of $\kappa_{AC}$. Since a theoretical curve $\tilde{\theta}_{nor,r}$ is not very sensitive to the change of $\kappa_{AC}$, even a minor correction of $\tilde{\theta}_{nor,e}$ can lead to large measurement errors.
The ideal $\theta_{\text{nor}, e}$ varies from 1 to 0.5 with increased $f$. However, in actual cases, $\theta_{\text{nor}, e}$ without a correction varies from 1 to a value slightly larger or smaller than 0.5 due to the relatively larger standard deviation at high frequencies as shown in Fig. 7.5 (a). Under the correction with parameter $C$, the distribution of $\theta_{\text{nor}, e}$ is stretched downward/upward to 0.5, which will give a lower/higher $\kappa_{\text{AC}}$. Obviously, $\theta_{\text{nor}, e}$ requiring little or no correction can generate a more accurate $\kappa_{\text{AC}}$. So, the measurement accuracy is fully determined by the quality of experimental data $\theta_{\text{nor}, e}$. For example, the 145.9-nm sample has $\kappa_{\text{AC}} = 13.5$ W m$^{-1}$ K$^{-1}$, which deviates from the rest severely. This large deviation in $\kappa_{\text{AC}}$ is indeed a result of the abnormal low quality of experimental data. The data quality is a result of the interaction of many factors, such as the gravity-induced deformation, the existence of micro-wrinkles/micro-bubbles, the temperature dependence of BP’s physical properties, as well as operation skills of researchers. However, how these factors influence the data quality is not yet fully understood, and more work is required to figure it out in future.

Based on the above analysis, we have developed useful strategies to optimize FR-Raman by suppressing measurement errors. For example, we can reduce the gravity-induced deformation by suspending a BP sample on a smaller square dent. Also, we can improve the modeling accuracy by considering the variation of BP’s physical properties with temperature in our thermal transport model. However, the modeling accuracy is improved at the expense of the simulation efficiency. So, how to balance the modeling accuracy and the simulation efficiency is a topic we should consider seriously in future work. Moreover, we can choose a laser with a longer wavelength as an energy source. A laser with a longer wavelength, e.g., 633 nm, is good for providing a clear and strong Raman spectrum but does not produce local heating as much as our current 532 nm laser.
Consequently, the signal-to-noise ratio of Raman spectrum can be improved, and the fitting error of $\theta_{nor,e}$ can be reduced. We believe these strategies can improve the measurement accuracy of FR-Raman and lay a foundation for its wide application in the future.
CHAPTER 8. FUTURE WORK AND CONCLUSION

8.1 Future Work

As a new technique for thermal characterization, we will continue to improve the measurement accuracy and capacity of FR-Raman. However, in the future, more of our efforts will be devoted to measurements of thermal properties of micro/nanomaterials. BP is one of important micro/nanomaterials that we will continue to study. Our previous FR-Raman experiments are performed on thick BP samples at room temperature. In fact, it is worthwhile to explore temperature effect and thickness effect on the anisotropic thermal conductivity of BP. The temperature effect can be studied by performing FR-Raman on BP samples at different temperatures. This can be easily achieved by changing BP samples’ temperature using the environmental cell in our Raman system. The study on thickness effect is more challenging since BP samples obtained from mechanical exfoliation are not thin enough to display thickness effect. For BP samples can be studied with FR-Raman, they must have large lateral size and uniform thickness. We have found a BP sample fabricated with mechanical exfoliation for a FR-Raman experiment cannot be thinner than 30 nm. Since thickness effect becomes apparent when a BP sample is thinner than 20 nm, these BP samples fabricated with mechanical exfoliation will not show any thickness effect. As a result, it is necessary to seek and employ a new method to prepare BP samples. So far, a photochemical etching method is perfectly suitable for preparing large and thin BP samples. This method utilizes reactive oxygen and water rinse to achieve a controlled layer-by-layer thinning of thick BP samples down to a single layer. Since this method can fabricate large BP samples with designed thickness, thickness effect on the anisotropic thermal conductivity of BP can be explored more
easily. The employment of FR-Raman can be easily extended to other two-dimensional materials, such as graphene, MoS$_2$ and WS$_2$. Except two-dimensional materials, FR-Raman has great potentials to be applied to study large varieties of micro/nanomaterials. By studying micro/nanomaterials with FR-Raman, database of thermal properties of micro/nanomaterials can be largely expanded. This will greatly contribute to potential applications of micro/nanomaterials in thermal management and electronic devices.

8.2 Conclusion

In this work, BP is studied thoroughly with nondestructive Raman-based techniques to identify its crystalline orientation and measures its interface thermal conductance and anisotropic in-plane thermal conductivity. The identification of crystalline orientation is achieved using OT-Raman. This technique utilizes $\Phi$ as an indicator to identify the crystalline orientation, which has the largest/smallest value when laser polarization is in the armchair/zigzag direction. Its physical mechanism originates from the anisotropic heating effect of a linearly polarized laser. So far, the robustness and reliability of this technique has been proved by studying BP samples with different thickness. It suggests that OT-Raman can identify the crystalline orientation of BP explicitly regardless of excitation wavelength and sample thickness. In fact, identifying crystalline orientation of BP is the prerequisite for measuring its interface thermal conductance and anisotropic in-plane thermal conductivity. In other words, the development of OT-Raman lays the foundation for following studies.

Exfoliated BP samples supported on Si substrate are studied with micro-Raman spectroscopy, from which interface thermal conductance between BP and its adjacent Si substrate can be measured. BP samples in a thickness range of 16.6-113.7 nm are studied
from 223 to 293 K. These measurements give high interface thermal conductance, which shows BP can be used as interface material for new generation of devices. With abundant experimental data, temperature effect and thickness effect on interface thermal conductance can also be explored. It is found that interface thermal conductance shows a strong negative correlation to temperature, while no correlation to thickness. The strong temperature dependence of interface thermal conductance results from the morphological variation of a supported BP sample with temperature. The independence of interface thermal conductance on thickness is related to the large variation in initial interface contact of supported BP samples, which overshadows the weak intrinsic thickness dependence. Successful application of micro-Raman spectroscopy requires to calculate absorbed laser power $P_0$ and calibrate Raman spectrum with temperature by measuring temperature coefficient $\chi$. We have found that $P_0$ and $\chi$ are two major parameters for inducing measurement errors in interface thermal conductance.

FR-Raman is developed to eliminate errors induced by $P_0$ and $\chi$. This new technique can achieve accurate and rapid thermal characterization without the knowledge of $P_0$ and $\chi$. This is contributed by using a square-wave laser as an energy source to induce heating effect and excite Raman scattering. The first FR-Raman is conducted on a c-Si cantilever to measure its thermal diffusivity. The c-Si cantilever has a reference value of thermal diffusivity, which can be used to verify the validity of FR-Raman. In fact, our measured thermal diffusivity agrees well with the reference value, which confirms the validity of FR-Raman. Then, FR-Raman is used to study the anisotropic in-plane thermal conductivity of BP. FR-Raman is perfectly suited for studying BP which has oxidation nature in air and relatively small sample size. Our measurements on BP
samples with thickness between 99.8 and 157.6 nm show the armchair thermal conductivity is 13.5–22 W m$^{-1}$ K$^{-1}$, and the zigzag thermal conductivity is 39.8–62.7 W m$^{-1}$ K$^{-1}$. These results are in good agreement with literature reports. Most importantly, this study demonstrates the potential of extending the application of FR-Raman to large varieties of micro/nanomaterials.

All these studies advance our fundamental understanding on the phonon transport and interaction in BP, which can further benefit future development of many technological applications, including electronics, optoelectronics and thermoelectrics.
REFERENCES


