Thickness-Dependent Thermal Conductivity of Suspended Boron Nitride (Postprint)

Authors: Guo Jie (1,2); Wang Chengru (1,2); Dong Lan (1,2); Xu Xiangfan (1,2,3)

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Abstract

This work investigates the in-plane thermal conductivity of multilayer suspended boron nitride. We obtain multilayer boron nitride via mechanical exfoliation and suspend it on a microbridge device using a dry transfer technique, subsequently performing thermal conductivity measurements. During the dry transfer process, we use polydimethylsiloxane (PDMS) as the boron nitride carrier, resulting in fewer residual organic contaminants on the sample surface and higher sample quality. This work measures the in-plane thermal conductivity of four-layer suspended boron nitride reaching 286 Wm-1K-1 at room temperature, which is comparable to the known thermal conductivity of bulk boron nitride but lower than that of bilayer boron nitride samples, thereby experimentally demonstrating that the in-plane thermal conductivity of suspended boron nitride exhibits a thickness dependence.

Full Text

Preamble

Thickness-Dependent Thermal Conductivity in Suspended Few-Layer Boron Nitride

Jie Guo[12], Cheng-Ru Wang[12], Lan Dong[12], Xiang-Fan Xu[123]*

[1]Center for Phononics and Thermal Energy Science, School of Physics Science and Engineering, Tongji University, Shanghai 200092, China
[2]China-EU Joint Lab for Nanophononics, Tongji University, Shanghai 200092, China
[3]Shanghai Key Laboratory of Special Artificial Microstructure Materials and Technology, School of Physics Science and Engineering, Tongji University, Shanghai 200092, China

Abstract

This paper investigates the in-plane thermal conductivity of suspended multilayer hexagonal boron nitride (h-BN). We obtained multilayer boron nitride flakes via mechanical exfoliation and suspended them on micro-bridge devices using a dry-transfer technique for thermal conductivity measurements. During the dry-transfer process, we employed polydimethylsiloxane (PDMS) as the boron nitride carrier, which minimizes organic residue on the sample surface and yields higher sample quality. Our work measured an in-plane thermal conductivity of 286 Wm ^{1}K ^{1} at room temperature for a four-layer suspended boron nitride sample, which is comparable to the known thermal conductivity of bulk boron nitride but lower than that of bilayer boron nitride samples. This experimentally demonstrates a thickness-dependent thermal conductivity in suspended boron nitride.

Keywords: hexagonal boron nitride (h-BN); dry-transfer method; thermal conductivity; thickness-dependent thermal conductivity

Introduction

Inspired by the discovery of graphene, researchers have continuously exploited mechanical exfoliation to obtain various two-dimensional materials, ushering in a new era of investigation. Black phosphorus, boron nitride, and transition metal dichalcogenides have all attracted significant attention. Among the numerous two-dimensional materials discovered to date, boron nitride possesses a structure most similar to graphene. Each layer consists of equal numbers of nitrogen and boron atoms forming a hexagonal honeycomb structure through sp^2 hybridization [1,2], with each layer being a single atomic layer approximately 0.334 nm thick. Boron nitride not only has a thickness comparable to graphene but also exhibits even better flatness. Meanwhile, the boron-nitrogen covalent bonds are similarly strong. Although boron nitride lacks a large -bond network, it still possesses intriguing physical properties, including strong mechanical performance, high thermal stability, and high thermal conductivity [3,4,5,6,7,8,9]. Structural differences, however, lead to significant disparities in electrical properties. Graphene' s unique zero Dirac point properties endow it with high carrier mobility and electrical conductivity, whereas boron nitride is an insulator and is primarily studied as a dielectric material. The flat surface of boron nitride enables graphene/boron nitride devices to achieve carrier mobilities twenty times higher than those of graphene devices on rougher silicon dioxide substrates, reaching maximum values at low temperatures [10,11,12]. Flat boron nitride has also been used to study quantum oscillations and the quantum Hall effect in two-dimensional black phosphorus [13]. Notably, reports indicate that the in-plane thermal conductivity of suspended bilayer boron nitride reaches 484

Wm ^{1}K ^{1} [2], demonstrating boron nitride’ s potential in thermal transport and highlighting the importance of research on its in-plane and interfacial thermal conduction [14,15].

Theoretical calculations based on the Boltzmann transport equation predict that the room-temperature thermal conductivity of monolayer hexagonal boron nitride can be as high as 600 Wm ^{1}K ^{1}, which is greater than experimental results for bilayer boron nitride and far exceeds the bulk boron nitride thermal conductivity range of 220–390 Wm ^{1}K ^{1} [14,16,17,18]. This theoretical result suggests that suspended multilayer boron nitride should exhibit a thickness-dependent thermal conductivity. Similarly, theoretical and experimental reports on graphene and graphite indicate that out-of-plane acoustic phonons in bulk graphite are suppressed by interlayer forces [9]. Consequently, the in-plane thermal conductivity of graphene shows a clear thickness dependence, with monolayer graphene having the highest thermal conductivity, which decreases as thickness increases and eventually approaches the bulk value. For boron nitride, however, experimental results demonstrating this thickness dependence have been lacking. Recent experimental work reports thermal conductivities of 243 Wm ^{1}K ^{1} for 9-layer boron nitride measured by the Raman laser method [6] and 360 Wm ^{1}K ^{1} for 11-layer boron nitride measured by the micro thermal bridge method [5]. In these studies, the thermal conductivity of boron nitride with substrates or surface impurities increased with layer number because wet-transfer or PMMA transfer methods leave numerous organic impurities and functional groups on the sample surface, which affect the measured thermal conductivity by enhancing phonon scattering from impurities [5,18]. Therefore, to investigate the intrinsic thermal conductivity of multilayer boron nitride and its thickness dependence, we have introduced the PDMS dry-transfer method.

In this work, we use suspended micro-bridge devices to measure the thermal conductivity of suspended four-layer boron nitride. During sample fabrication, we employed the PDMS dry-transfer method to achieve cleaner sample surfaces. By measuring the in-plane thermal conductivity of suspended four-layer boron nitride and comparing it with bulk and bilayer boron nitride thermal conductivities, we verify the thickness-dependent characteristic that boron nitride’ s in-plane thermal conductivity decreases with increasing thickness.

1. Fabrication of Suspended Boron Nitride Samples

We first obtained four-layer boron nitride samples on transparent solid PDMS via mechanical exfoliation and characterized the sample morphology using an optical microscope to locate the boron nitride flakes (Fig. 1a [Figure 1: see original paper]). We then selected a suspended micro-bridge device with appropriate dimensions for sample transfer. The suspended micro-bridge device consists of two suspended platforms, each composed of platinum/silicon nitride bilayer films. One platform serves as the heater electrode (Fig. 1b Heater), while the other functions as the temperature sensor electrode (Fig. 1b Sensor). Six Pt/SiNx arms support the heater and sensor, enabling them to become suspended after wet etching removes the silicon substrate [2,3,19]. Subsequently, under an optical microscope, we placed the PDMS with the boron nitride sample facing downward, aligned the sample with the suspended micro-bridge device, gently pressed the PDMS onto the device, and removed the PDMS to successfully transfer the sample onto the suspended micro-bridge device (Fig. 1b, c). Finally, to ensure good contact between the sample ends and the electrodes and to further reduce the influence of residual impurities on the sample, we annealed the sample in a hydrogen/argon tube furnace at 500 K for two hours.

Raman spectroscopy is a common method for characterizing the layer number of two-dimensional materials. The layer number of MoS samples, for instance, is determined by Stokes peak shifts with sample thickness [20,21]. However, since the Stokes peak shift of boron nitride samples is not obvious with thickness variation [22], Raman spectroscopy is not suitable for determining boron nitride thickness. Atomic force microscopy can measure the thickness of two-dimensional materials, but because suspended micro-bridge devices vibrate during scanning, it is also unsuitable for determining boron nitride layer number in this experiment. Therefore, we used optical microscopy to characterize sample thickness, determining the layer number to be four based on imaging contrast on the substrate.

2. Thermal Bridge Measurement Method

Figure 1c shows a scanning electron microscopy (SEM) image of the suspended micro-bridge device, where the rectangular gray region between the heater and sensor represents the measured sample. Measurements were conducted in a JANIS variable-temperature system with chamber pressure below 1×10   Pa. Before measurement, the system was heated to 420 K and stabilized for over three hours to remove water molecules from the sample surface.

The platinum wires on the heater and sensor function as resistance thermometers. We can calibrate temperature changes by measuring the resistance curves of the platinum wires. When the system reaches thermal steady state and establishes a stable heat flux distribution, the thermal conductance of the Pt/SiNx arms (_b) and the sample (_s) can be calculated using the following formula [21]:

$$\Delta + \Delta \ \Delta - \Delta$$

where Q_h and Q_b are the Joule heating powers applied to the heater and Pt/SiNx arms, respectively, and ΔT_h and ΔT_s are the temperature changes on the heater and sensor, which are obtained from resistance changes in the heater and sensor.

In this work, the experimentally measured temperature changes represent the average temperature variations within the heater and sensor platforms, not the actual temperature changes at the sample ends. When calculating sample thermal conductance using the above formula, large errors can arise from the ΔT_h - ΔT_s term if the sample's total thermal conductance is substantial, significantly affecting the results. Therefore, after experimentally measuring the temperature difference, we corrected it using finite element analysis (COMSOL Multiphysics 5.2, License No: 9400382) before calculating thermal conductance [23].

We performed finite element simulations of the temperature distribution on the heater and sensor and present the simulation results at T = 300 K (Fig. 2a [Figure 2: see original paper] and 2b). Combining experimental measurement data, Fig. 2b shows the temperature distribution within the sensor platform: when the temperature change at the sample edge is 4.797 K, the measured average temperature change in the experiment is 4.709 K. A similar temperature difference exists in the heater electrode. We applied corrections at each measured temperature point. At T = 300 K, the difference between corrected and uncorrected thermal conductance results is 4.8%.

3. Measurement Results and Analysis

The total thermal resistance (R_s) of the boron nitride sample consists of two contributions: the intrinsic thermal resistance of the suspended portion (R_BN) and the contact thermal resistance at the sample ends with the heater and sensor (R_c), i.e., R_s = R_BN + 2R_c. The contact thermal resistance can be calculated using the following formula:

tanh

where _BN is the thermal conductivity of boron nitride, w is the width of boron nitride, t is the thickness of boron nitride, A is the contact area between the sample and suspended platforms, L_c is the contact length, and g_int is the interfacial thermal conductance per unit contact area between the boron nitride sample and the heater/sensor. Since experimental reports on boron nitride/platinum interfacial thermal resistance are scarce and wet-transfer methods introduce many impurities at the interface with significant effects, we 引用 data for clean boron nitride/silicon dioxide interfacial thermal conductance [15]. Through calculation, we determined that the contact thermal resistance accounts for 6.5% of the total thermal resistance (2R_c/R_s) at 300 K and 3.9% at 60 K. These results indicate that the influence of contact thermal resistance on thermal conductivity in this work is essentially negligible.

We present the temperature-dependent thermal conductivity of the four-layer suspended boron nitride sample (Fig. 3a). The sample' s thermal conductivity can be calculated using = l/wt, where l = 3 m is the sample length, w = 2.2 m is the sample width, and t = 1.336 nm is the sample thickness [2,25]. The thermal conductivity varies with temperature, peaking at T = 240 K. As temperature increases, three-phonon Umklapp scattering gradually dominates, causing the thermal conductivity to decrease. The room-temperature thermal conductivity is 286 Wm ^{1}K ^{1}, which falls within the range of high-quality bulk boron nitride thermal conductivity [14,26]. When T < 80 K, the sample’ s thermal conductance exhibits a temperature dependence of T^2.53±0.12 after fitting (Fig. 3b). Boron nitride’ s thermal conduction behavior is similar to that of graphene. For monolayer graphene, ballistic thermal conductance at low temperatures shows a T^1.5 dependence [27]. As graphene thickness increases, phonon diffusion occurs in the out-of-plane direction, causing bulk graphite’ s low-temperature thermal conductance to exhibit a T^2.5 dependence. With four layers of boron nitride in this work, the vertical phonon velocity is minimized under low-frequency constraints, leading to a temperature dependence similar to bulk materials. Our results also resemble the theoretical temperature dependence of bulk graphite thermal conductance at low temperatures.

To further demonstrate that the thermal conduction behavior of our four-layer boron nitride sample is similar to bulk boron nitride, we selected the sample’ s in-plane thermal conductivity at T = 300 K and compared it with theoretical monolayer values, experimental bilayer results, and bulk boron nitride thermal conductivity. The layer-number dependence of two-dimensional material thermal conductivity has been an important topic of interest in recent years. Theoretical and experimental work has demonstrated that due to interlayer scattering, the thermal conductivity of clean suspended graphene samples decreases with increasing thickness [8,30]. Boron nitride’s structure is very similar to graphene, and its thermal conductivity is theoretically expected to show similar thickness dependence [8,30]. By comparing thermal conductivities of boron nitride samples with different thicknesses at T = 300 K (Fig. 3c [Figure 3: see original paper]), we find that our measured four-layer boron nitride thermal conductivity is lower than both theoretical monolayer boron nitride and experimental bilayer values, while falling within the bulk boron nitride room-temperature thermal conductivity range of 200-390 Wm ^{1}K ^{1}. This confirms that boron nitride thermal conductivity decreases with increasing layer number. The four-layer sample’ s thermal conductivity does not reach the maximum bulk value of 390 Wm ^{1}K ^{1}, primarily due to variations in boron nitride quality across different studies.

Conclusion

This work measured the thermal conductivity of a four-layer suspended boron nitride sample using the thermal bridge method. We employed PDMS-mediated dry-transfer to obtain relatively higher-quality samples with fewer surface contaminants. The sample’ s thermal conductivity reaches 286 Wm ^{1}K ^{1} at room temperature, within the range of bulk boron nitride thermal conductivity, and exhibits a low-temperature temperature dependence approaching T^2.5. By comparing our sample’ s thermal conductivity at 300 K with values for boron nitride of different thicknesses, we confirmed the thickness-dependent characteristic that boron nitride thermal conductivity decreases with increasing thickness. This work provides a foundation for further investigation of boron nitride' s thermal transport properties.

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Contact Information:
Room 505, Building 1, South Campus, Tongji University, 67 Chifeng Road, Yangpu District, Shanghai
Mobile: 18019787122
Phone: 021-65983429
Email: xuxiangfan@tongji.edu.cn

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