Postprint: Thickness-Dependent Thermal Conductivity of Suspended Boron Nitride

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Date: 2017-11-07T00:00:00+00:00

Abstract

This study investigates the in-plane thermal conductivity of multilayer suspended boron nitride. Multilayer boron nitride flakes are obtained via mechanical exfoliation and subsequently suspended on microbridge devices using dry transfer technique for thermal conductivity measurements. During the dry transfer process, polydimethylsiloxane (PDMS) is employed as the carrier for boron nitride, which minimizes residual organic contaminants on the sample surface and enhances sample quality. This work measures an in-plane thermal conductivity of 286 $Wm^{-1}K^{-1}$ at room temperature for four-layer suspended boron nitride, a value comparable to that of bulk boron nitride but lower than that of bilayer boron nitride samples, thereby experimentally demonstrating a thickness-dependent effect on the in-plane thermal conductivity of suspended boron nitride.

Full Text

Preamble

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

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Abstract

This paper investigates the in-plane thermal transport properties of exfoliated few-layer hexagonal boron nitride (h-BN). By combining a PDMS-mediated dry-transfer method with the thermal bridge technique, we successfully obtained high-quality samples suitable for thermal conductivity ( ) measurement. This dry-transfer approach helps reduce polymer residue on the sample surface. The measured thermal conductivity reaches approximately 286 $\mathrm{Wm^{-1}K^{-1}}$ at room temperature in a four-layer h-BN sample. We found that this value is comparable to that of bulk h-BN but lower than that of bilayer samples, indicating a thickness-dependent thermal conductivity in suspended few-layer boron nitride. This result is consistent with low-temperature measurements showing that   increases with temperature as $\sim T^{2 \cdot 53} \pm ^{0 \cdot 12}$, suggesting bulk-like behavior in the four-layer h-BN sample.

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

Introduction

Inspired by the discovery of graphene, researchers have increasingly employed 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 one atomic sheet 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 spatially extended π bonds are absent, these materials still possess intriguing physical properties, including exceptional mechanical performance, high thermal stability, and substantial thermal conductivity [3,4,5,6,7,8,9].

Of course, subtle structural differences lead to significant disparities in electrical properties. Graphene’ s unique zero Dirac point characteristics endow it with high carrier mobility and excellent electrical conductivity, whereas boron nitride is an insulator that has been studied primarily as a dielectric material. The atomically flat surface of boron nitride enhances carrier mobility in graphene/BN devices by twentyfold compared to graphene devices on rougher SiO_2 substrates, reaching maximum values at low temperatures [10,11,12]. This flatness has also enabled investigations of quantum oscillations and the quantum Hall effect in two-dimensional black phosphorus [13]. Additionally, it is particularly noteworthy that the reported in-plane thermal conductivity of suspended bilayer boron nitride reaches 484 $\mathrm{Wm^{-1}K^{-1}}$ [2], demonstrating boron nitride’ s potential for thermal transport applications and highlighting the importance of research on both in-plane and interfacial thermal conduction in boron nitride [14,15].

Theoretical calculations based on the Boltzmann transport equation predict that the room-temperature thermal conductivity of monolayer hexagonal boron nitride could be as high as 600 $\mathrm{Wm^{-1}K^{-1}}$, exceeding experimental results for bilayer boron nitride and far surpassing the bulk boron nitride thermal conductivity range of 220-390 $\mathrm{Wm^{-1}K^{-1}}$ [14,16,17,18]. These theoretical results suggest 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, graphene’ s in-plane thermal conductivity shows a clear thickness dependence, with monolayer graphene having the highest thermal conductivity that decreases with increasing thickness and eventually approaches the bulk value. For boron nitride, however, experimental evidence of thickness-dependent thermal conductivity has been lacking. Recent experimental work reported thermal conductivities of 243 $\mathrm{Wm^{-1}K^{-1}}$ for 9-layer boron nitride measured by the Raman laser method [6] and 360 $\mathrm{Wm^{-1}K^{-1}}$ for 11-layer boron nitride measured by the micro thermal bridge method [5]. In these studies, the thermal conductivity of boron nitride on substrates or with surface impurities increased with layer number. This occurs because wet-transfer or PMMA-transfer methods leave numerous organic contaminants 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 measured the thermal conductivity of suspended four-layer boron nitride using a suspended micro-bridge device. During sample fabrication, we employed the PDMS dry-transfer method to achieve a cleaner sample surface. 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 experimentally verify that the in-plane thermal conductivity of suspended boron nitride decreases with increasing thickness.

1. Fabrication of Suspended Boron Nitride Samples

We first obtained four-layer boron nitride samples on transparent solid PDMS by mechanical exfoliation and characterized the sample morphology using optical microscopy to locate the boron nitride samples (Fig. 1a [Figure 1: see original paper]). We then selected an appropriate suspended micro-bridge device for sample transfer. The suspended micro-bridge device features two suspended platforms, each composed of platinum/silicon nitride bilayer membranes. 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 (Figs. 1b,c). Finally, to ensure good contact between the sample ends and the electrodes and to further reduce the influence of impurity residues, we annealed the sample in a hydrogen/argon tube furnace at 500 K for two hours.

Figure 1: (a) Four-layer boron nitride sample mechanically exfoliated on PDMS; (b) Optical microscope image after transferring the boron nitride sample onto the device; (c) Scanning electron microscope image showing the device morphology, with the suspended portion of the boron nitride sample measuring 3 m in length and 2.2 m in width. Scale bar: 15 m.

Raman spectroscopy is a common method for characterizing the layer number of two-dimensional materials. For example, the layer number of MoS_2 samples is determined by Stokes peak shifts with sample thickness [20,21]. However, since the Stokes peak shift in 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 the suspended micro-bridge device vibrates during scanning, making AFM unsuitable for thickness determination in this experiment. Therefore, we used optical microscopy to characterize sample thickness by utilizing imaging contrast on the substrate to determine the layer number.

2. Thermal Bridge Measurement Method

Figure 1c shows a scanning electron microscope (SEM) image of the suspended micro-bridge device, where the rectangular gray region between the heater and sensor represents the measured sample. Measurements were performed in a JANIS variable-temperature system with chamber pressure below 1$×10^{-5}$ Pa. Before measurement, the system was heated to 420 K for over three hours to remove water molecules from the sample surface.

The platinum wires on the heater and sensor function as resistance thermometers. By measuring the resistance curves of the platinum wires, we can calibrate the corresponding temperature changes. When the system reaches thermal steady state and establishes a stable heat flow distribution, the thermal conductance of the Pt/SiNx arms (σb) and the sample (σs) can be calculated using the following formulas [21]:

$$\sigma_b = \frac{Q_h}{\Delta T_h + \Delta T_s}$$

$$\sigma_s = \frac{Q_h + Q_b}{\Delta T_h - \Delta T_s}$$

where Qh and Qb are the Joule heating powers applied to the heater and Pt/SiNx arms, respectively, and ΔTh and ΔTs are the temperature changes on the heater and sensor, which can be obtained from resistance changes.

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 using these formulas to calculate sample thermal conductance, large errors can arise if the sample' s total thermal conductance is substantial, as the error in ΔTh-ΔTs increases significantly. Therefore, after experimentally measuring the temperature differences, we corrected them using finite element analysis (COMSOL Multiphysics 5.2, License No: 9400382) before calculating the thermal conductance [23].

We performed finite element simulations of the temperature distribution on the heater and sensor platforms and present the simulation results at T=300 K (Figs. 2a [Figure 2: see original paper] and 2b). Combining the simulation with experimental data, Fig. 2b shows the temperature distribution within the sensor platform: when the temperature change at the sample edge is 4.797 K, the experimentally measured average temperature change is 4.709 K. A similar temperature difference exists in the heater platform. We applied this correction at every measured temperature point. At T=300 K, the thermal conductance results differ by 4.8% before and after correction.

Figure 2: Finite element analysis (COMSOL Multiphysics 5.2) of temperature distribution. (a) Temperature distribution of the suspended thermal bridge device at 300 K; (b) Temperature profile along the thick solid line in Fig. 2a at 300 K.

3. Measurement Results and Analysis

The total thermal resistance (Rs) of the boron nitride sample comprises two contributions: the intrinsic thermal resistance of the suspended portion (RBN) and the contact resistance at both ends where the sample meets the heater and sensor (Rc), such that Rs = RBN + 2Rc. The contact resistance can be calculated using the following formula [24]:

$$R_c = \frac{1}{\sqrt{\kappa_{BN} w t g_{int}}} \tanh\left(\frac{L_c}{\sqrt{A/(wtg_{int})}}\right)$$

where BN is the thermal conductivity of boron nitride, w is the width, t is the thickness, A is the contact area between the sample and suspended platforms, Lc is the contact length, and gint is the interfacial thermal conductance per unit contact area between the boron nitride sample and the heater/sensor. Since experimental reports on the interfacial thermal resistance of boron nitride/platinum contacts are scarce and wet-transfer interfaces contain many impurities that significantly affect the results, we used interfacial thermal conductance data for clean boron nitride in contact with SiO_2 [15]. Our calculations show that the contact resistance accounts for 6.5% of the total resistance (2Rc/Rs) at 300 K and 3.9% at 60 K, indicating that contact resistance effects are negligible in this work.

We present the temperature-dependent thermal conductivity of the four-layer suspended boron nitride sample (Fig. 3a [Figure 3: see original paper]). The sample' s thermal conductivity can be calculated using = σl/wt, where l = 3 m is the sample length, w = 2.2 m is the width, and t = 1.336 nm is the 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. At room temperature, the thermal conductivity is 286 Wm^{-1}K^{-1}, which falls within the range of high-quality bulk boron nitride thermal conductivity [14,26]. For T $<$ 80 K, the thermal conductivity exhibits a temperature dependence of T$^{2\cdot53}\pm^{0\cdot12}$ after fitting (Fig. 3b). Boron nitride and graphene show similar thermal transport behavior. For monolayer graphene, ballistic thermal transport at low temperatures follows a T$^{1\cdot5}$ dependence [27]. As graphene thickness increases, phonon diffusion occurs in the out-of-plane direction, leading to a T$^{2\cdot5}$ temperature dependence for bulk graphite at low temperatures. Our four-layer boron nitride sample, under low-frequency constraints where the out-of-plane acoustic velocity is minimal, exhibits a temperature dependence similar to bulk material. Our results also align with theoretical predictions for the low-temperature temperature dependence of bulk graphite thermal conductivity.

To further demonstrate that the thermal transport behavior of our four-layer boron nitride sample resembles that of bulk boron nitride, we compared its in-plane thermal conductivity at T = 300 K with theoretical monolayer values, experimental bilayer results, and bulk boron nitride thermal conductivity. The layer-number dependence of in-plane thermal conductivity in two-dimensional materials has been an important research topic in recent years. Theoretical and experimental work has shown that due to interlayer scattering effects, the thermal conductivity of clean suspended graphene decreases with increasing thickness [28,29]. The thickness dependence of boron nitride thermal conductivity remains controversial, primarily due to the lack of experimental results. 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), we find that our measured four-layer boron nitride thermal conductivity is lower than both the theoretical monolayer value and the experimental bilayer result, 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}, mainly due to variations in boron nitride quality across different studies.

Figure 3: (a) Temperature dependence of in-plane thermal conductivity for

four-layer boron nitride; (b) Low-temperature ballistic transport thermal conductivity of four-layer boron nitride as a function of temperature; (c) Thickness dependence of thermal conductivity in hexagonal boron nitride samples.

Conclusion

In this work, we measured the thermal conductivity of a four-layer suspended boron nitride sample using the thermal bridge method. We employed PDMS dry-transfer to obtain relatively higher-quality samples. The sample' s thermal conductivity reaches 286 $\mathrm{Wm^{-1}K^{-1}}$ at room temperature, within the range of bulk boron nitride thermal conductivity, and shows a near-$\mathrm{T}^{2\cdot 5}$ temperature dependence at low temperatures. By comparing this sample' s thermal conductivity at 300 K with boron nitride samples of different thicknesses, we demonstrated the thickness-dependent characteristic of decreasing thermal conductivity with increasing layer number. This work provides a foundation for further investigation of thermal transport in boron nitride.

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