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Analysis of the anomalies in graphene thermal properties

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ABSTRACT

A comprehensive analysis of the thermal conductivity of graphene under various conditions is presented in this study. Results obtained from different experimental and theoretical methods are analyzed and discussed for numerous conditions such as preparation process, shape, sample size, wavelength, and temperature. Wide discrepancies in the measured thermal conductivity results were found in many studies in the literature. Based on the cited data for the graphene thermal conductivity, the initially measured thermal conductivities appear to be highly overestimated. Majority of the documented results reported lower values of thermal conductivity than the earlier reported results. Furthermore, large differences in the values of the thermal conductivity of graphene were noticed from the cited results using different experimental and numerical methods (0.14 W/m K–20,000 W/m K). This raised an important question on the accuracy of these methods when measuring thermal conductivity of graphene at nanoscale. We have established the existence of a high degree of anomalies in the value of the thermal conductivity of grapheme. Therefore, proper experimental and theoretical studies should be conducted to accurately measure the thermal conductivity of graphene.

1. Introduction

Graphene, a single layer of carbon atoms bonded in a hexagonal lattice, is considered an excellent conductor of heat and electricity. Among its significant properties, an extremely high thermal conductivity, it has received voluminous attention in scientific and industrial fields over the last decade both experimentally and theoretically [1–12]. This consideration stems from its importance in a variety of important applications such as thermal management and electronic interconnects application [1–4,13–30].

There have been several works discussing the topic of graphene in recent years. For example, Castro Neto et al. [3] considered the basic theoretical aspects of graphene with unusual two-dimensional Dirac-like electronic excitations. Ma et al. [31] focused on recent progress in the synthesis of graphene nanoribbons (GNRs) by different techniques, especially longitudinal unzippling of carbon nanotubes (CNTs). The mechanical, electronic, and magnetic properties and edge reconstruction of GNRs are briefly summarized as well. Choi et al. [32] presented a study on the advancement of research in graphene, in the area of synthesis, properties and applications such as field emission, sensors, electronics, and energy, the limitations of present knowledge base and future research directions. A study of fundamental electronic properties of two-dimensional graphene with an emphasis on density and temperature-dependent carrier transport in doped or gated graphene structures was provided by Das Sarma [33]. The main feature of that work was a critical comparison between carrier transport in graphene and two-dimensional semiconductor systems (e.g., hetero-structures, quantum wells, inversion layers) so that the unique features of graphene electronic properties arising from its gapless, mass-less, chiral Dirac spectrum were highlighted.

Zhang et al. [34] summarized the recent advances in the study of graphene edges, including edge formation energy, edge reconstruction, method of graphene edge synthesis and the recent progress on metal-passivated graphene edges and the role of edges in graphene CVD growth. The aim of their work was to provide a guideline for readers to gain a clear picture of graphene edges from several aspects, especially the catalyst-passivated graphene edges and their role in graphene CVD growth. Recently, Renteria et al. [35] considered the thermal properties of graphene, few-layer graphene and graphene nanoribbons, and discussed practical applications of graphene in thermal management and energy storage. It was shown that the use of liquid-phase-exfoliated graphene as filler material in phase change materials was promising for thermal management of high-power-density battery packs.

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However, the thermal conductivity measurements of graphene reported to date exhibited contradictory results. For example, Balandin et al. [12] and Ghosh et al. [36] reported that the thermal conductivity of graphene measured by Raman Spectroscopy were 4840–5300 W/m K (2–5 μm diameter) and ∼3080–5150 W/m K (1–5 μm diameter), respectively. On the other hand, Lee et al. [37] reported that the thermal conductivity of a suspended pristine graphene measured by the same method was ranging from ∼1800 W/m K near 325 K to ∼710 W/m K at 500 K. Moreover, Faugeras et al. [11] reported that the thermal conductivity of a suspended graphene disk 44 μm in diameter measured by the same method was 632 W/m K. Although the diameter of the suspended disk used by Faugeras et al. [11] was about nine times the diameter of the graphene used by Balandin et al. [12], the conductivity obtained by Faugeras et al. was about eight times smaller than that obtained by Balandin et al. [12]. Other experimental methods such as microelectrothermal system and scanning thermal microscopy reported values of graphene thermal conductivity in the range of 10–2500 W/m K [38–40,5,41–47]. On the theoretical side, the picture is equally open with estimates varying in an even larger range of thermal conductivity values between 25 and 20,000 W/m K [48,49,40,50–55]. This clearly shows great disagreements in the reported results of graphene thermal conductivity in the literature.

The aim of this investigation is to analyze the discrepancies in the reported thermal conductivity of graphene using different experimental and theoretical techniques. Also, the accuracy of the initially reported thermal conductivity in the literature will be discussed.

2. Experimental methods of measuring thermal conductivity of graphene

Various experimental techniques were used in the literature to measure the thermal conductivity of graphene such as Raman spectroscopy, microelectrothermal system, and scanning thermal microscopy. In what follows, we will elucidate the discrepancies in the measured results of thermal conductivity of graphene.

2.1. Raman spectroscopy

Raman spectroscopy of graphene has received considerable attention since the discovery of graphene [56,57]. Chen et al. [56] measured the thermal conductivity of a graphene monolayer grown by chemical vapor deposition and suspended over holes with different diameters using micro-Raman spectroscopy. The obtained thermal conductivity values of the suspended graphene ranged from (2.6 ± 0.9) to $(3.1 \pm 1.0) \times 10^3$ W/m K near 350 K without showing the sample size dependence predicted for suspended, clean, and flat graphene crystal. Lee et al. [37] measured the thermal conductivity of suspended single-layer graphene as a function of temperature using Raman scattering spectroscopy on clean samples prepared directly on a pre-patterned substrate by mechanical exfoliation without chemical treatments. Thermal conductivity was deduced by analyzing the heat diffusion equation assuming that the substrate is a heat sink at an ambient temperature. The obtained thermal conductivity values range from ∼1800 W/m K near 325 K to ∼710 W/m K at 500 K. Cai et al. [6] measured room-temperature thermal conductivity of $(370 + 650/-320)$ W/m K for the supported graphene. The thermal conductivity of the suspended graphene exceeds $(2500 + 1100/-1050)$ W/m K near 350 K and becomes $(1400 + 500/-480)$ W/m K at about 500 K. Jauregui et al. [57] conducted an experimental study to determine the thermal conductivity of graphene using Raman spectroscopy. The thermal conductivity of suspended CVD graphene was in the range of 1500–5000 W/m K using Raman spectroscopy.

Table 1 illustrates measured thermal conductivity values of graphene for various conditions using Raman spectroscopy method. It can be seen from this table that there is large discrepancies in the measured thermal conductivity results. For example, Balandin et al. [12] reported a value of 4840–5300 W/m K for graphene at room temperature, which seems to be substantially higher than those measured by a number of other investigators. On the other hand, Faugeras et al. [11] reported thermal conductivity of 632 W/m K at 660 K for exfoliated graphene which is close to the results reported by Lee et al. [37] at 500 K (∼710 W/m K). The most important difference between the analysis of Balandin et al. [12] and the work of Lee et al. [37] and others is the value of the absorptance α of single layer graphene. Balandin et al. [12] used $\alpha = 13\%$, which is several times larger than the value of 2.3% measured and theoretically analyzed by Nair et al. [58]. If one uses $\alpha = 2.3\%$, their thermal conductivity value would reduce to 940 W/m K. Chen et al. [56] measured the thermal conductivity of a graphene monolayer grown by chemical vapor deposition and suspended over holes with different diameters ranging from 2.9 to 9.7 μm measured in vacuum using Raman spectroscopy. The obtained thermal conductivity values of the suspended graphene was ranging from (2.6 ± 0.9) to $(3.1 \pm 1.0) \times 10^3$ W/m K near 350 K.

Table 1 also demonstrates disagreements in the results associated with the effect of sample size on the thermal conductivity of graphene. For example, Ghosh et al. [36] and Balandin et al. [12] showed that as the diameter of the sample increases, the thermal conductivity increases. However, Chen et al. [56] illustrated that the thermal conductivity of graphene does not depend on the size of the sample. The results presented by Lee et al. [37] confirmed this finding. Fig. 1 demonstrates a wide dispersion of thermal conductivity of single layer graphene across various sample size using Raman Spectroscopy technique at room temperature. The sample size appears not correlating with thermal conductivity results of graphene. Therefore, this area of research would benefit from further studies which adhere to standard set of parameters to produce precise estimate of thermal conductivity of graphene. Lee et al. [37] showed that the thermal conductivity of graphene is strongly temperature dependent. As the temperature increases, the thermal conductivity of graphene decreases using the Raman Spectroscopy method. Using results from different studies in the literature, Fig. 2 illustrates the effect of varying the temperature on the thermal conductivity of single layer graphene using Raman spectroscopy. This figure clearly shows that as the temperature increases, the thermal conductivity of graphene decreases.

2.2. Microelectrothermal systems

Microelectrothermal systems have been used in recent years to measure the thermal conductivity of graphene [38,5,41–43,64,65]. Seol et al. [41] developed a nanofabricated resistance thermometer device to measure the thermal conductivity of graphene monolayers exfoliated onto silicon dioxide. The measurement results indicated that the thermal conductivity of the supported graphene was approximately 600 W/m K at room temperature. Dorgan et al. [42] studied the intrinsic transport properties of suspended graphene devices at high potential gradient fields and high temperatures ($\geqslant$1000 K). Their results revealed that the thermal conductivity of graphene was 2500 W/m K at room temperature and 310 W/m K at 1000 K. Bae et al. [64] illustrated experimentally a decrease of the thermal conductivity as the width reduced to a size regime comparable to the intrinsic phonon mean free path. For instance, at room temperature, thermal conductivity ∼230, 170, 100, and 80 W/m K was observed for graphene nanoribbons (GNRs) of width ∼130, 85, 65, and 45 nm, respectively. Xu et al. [40] reported measurements of thermal conduction in suspended single layer graphene (SLG) grown by chemical vapor deposition