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研究課題名（和文）グラフェンヒートスプレッダーの開発を目的としたグラフェン－基板界面効果の解明

研究課題名（英文）Study of graphene interfacial effect for the development of nano heat spreader

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研究成果の概要（和文）：グラフェンは極めて高い熱伝導率を有し，電子デバイスのヒートスプレッダーとしての利用が期待されている．しかし，グラフェンの熱輸送性質は界面効果の影響を大きく受け，性能が大きく低下する可能性がある，その界面効果の定量的に明らかにすることが必要．本研究は，T型とH型MEMSデバイスを利用して，単層懸架グラフェンリボンの熱伝導率を計測しました．基板を支えるグラフェンより，懸架グラフェンの熱伝導率は非常に高い，2000W/mK以上です．グラフェン界面フォノン散乱の重要な影響を解明しました．

研究成果の概要（英文）：Graphene have ultrahigh thermal conductivity, making it a promising material for spreading waste heat from the hotspot to the heat sink. However, the interfacial effect has significant influence on the thermal conductivity of graphene, it may greatly reduce the performance of the graphene heat spreader. It is necessary to investigate the interfacial effect between graphene and substrate quantitatively. In this project, we used T-type and H-type sensors to measure the thermal conductivity of suspended graphene. Comparing with the supported graphene on substrate (600 W/mK), the suspended graphene has much higher thermal conductivity, over 2000 W/mK. It demonstrates that the interfacial phonon scattering has dominant effect on the thermal conductivity of graphene.

研究分野： 工学

キーワード： suspended graphene　thermal conductivity　substrate effect　heat spreader　width dependence

１．研究開始当初の背景

Graphene has ultrahigh thermal conductivity, which makes it the one of the most promising materials for spreading waste heat from the local hotspot to the surrounding heat sinks. However, people have found that the supported graphene may have much lower thermal conductivity due to the strong interfacial interaction with the substrate. On the other hand, graphene is usually supported on the substrate in real applications because of its extremely small thickness. Hence, the strong interfacial effect of graphene needs to be investigated quantitatively for designing and fabricating new graphene heat spreaders.

Although the interfacial effect is dominant for the heat conduction in graphene, the available experimental data are quite few due to the next two reasons: (1) The experimental data are rather scattered due to the measurement difficulty of one-atom thick graphene membrane. The optical Raman method is usually used for measuring the thermal conductivity of graphene, but the measurement accuracy is quite limited due to the low temperature sensitivity of Raman peak shift. The uncertainty could be larger than 20% [1]. (2) The same measurement method of thermal conductivity is necessary for examining the interfacial effect. Because the thermal measurement result of graphene depends on the applied method, size and quality of sample, temperature range, etc, it is difficult to investigate the role of interfacial effect by comparing the results obtained by different methods. The measurement uncertainty may cover the difference caused by the interfacial effect.

From this point of view, we need to develop a more accurate method to measure the thermal conductivity of graphene and examine the interfacial effect on the heat conduction in graphene.

２．研究の目的

The purpose of this project is to develop an accurate method for measuring the thermal conductivity of graphene and understand the role of interfacial effect quantitatively. We have developed a new T-type sensor for measuring the suspended monolayer graphene. The uncertainty is around 5%, much smaller than the optical Raman method. Then, the interfacial effect of graphene can be understood quantitatively by comparing the results of graphene samples with and without substrate.

３．研究の方法

Firstly, we have developed a new method for preparing the suspended graphene device, which is the foundation for performing thermal measurement. The flowchart of MEMS process is given in the Fig. 1: (1) The CVD graphene is transferred onto the smooth SiO_2/Si substrate. Then the graphene is cut into micro ribbon by using standard EB lithography and O_2 plasma etching. (2) The metal sensor and electrode are deposited on graphene by using EB lithography and lift off technique. (3) Third EB lithography is used to make protection layer on top of graphene and open etch windows. (4) The SiO_2 layer and Si substrate are etched by using buffered hydrofluoric acid and XeF_2 gas reaction. The whole graphene device is suspended from the substrate. (5) The protection layers at both sides of graphene are removed. The graphene is suspended between two metallic sensors.

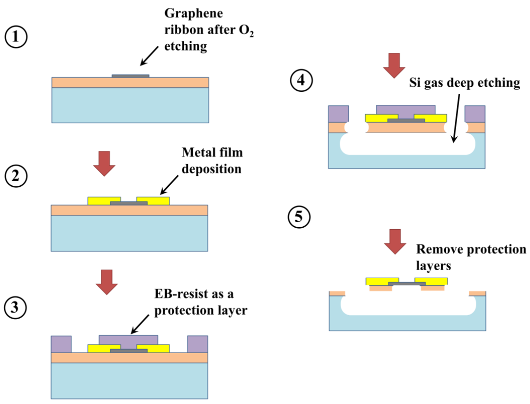

Fig. 1 Flowchart of MEMS process

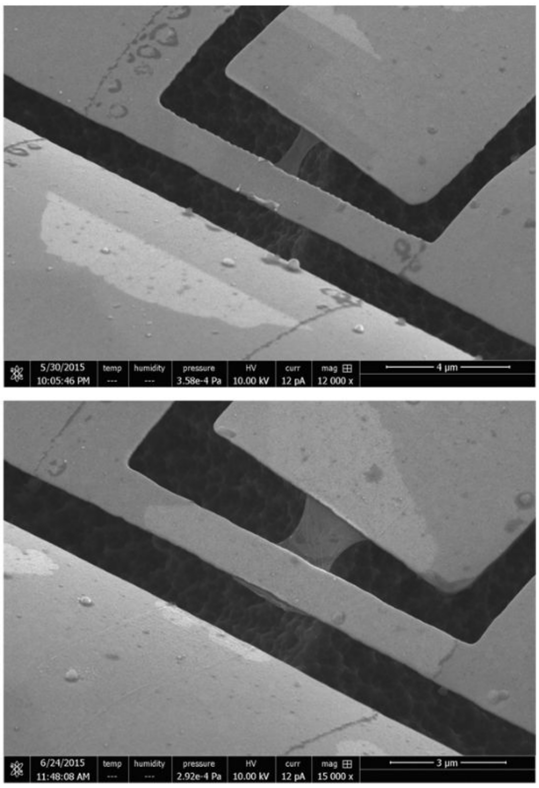

Fig. 2 SEM images of suspended graphene

Figure 2 shows the SEM images of some suspended graphene samples. It is seen that the suspended graphene ribbon bridges between the metallic sensor and heat sink. The graphene sample, metallic sensor and part of heat sink are suspended from the substrate. The metallic sensor is made of 100nm Au film.

Secondly, the thermal conductivity of graphene ribbon can be measured by using T-type or H-type method. The metallic sensor is used as Joule heater and precise resistance thermometer at the same time. The temperature change of sensor can be obtained by measuring its resistance change. In contrast to the optical Raman method, the MEMS sensor has much higher temperature sensitivity and higher accuracy.

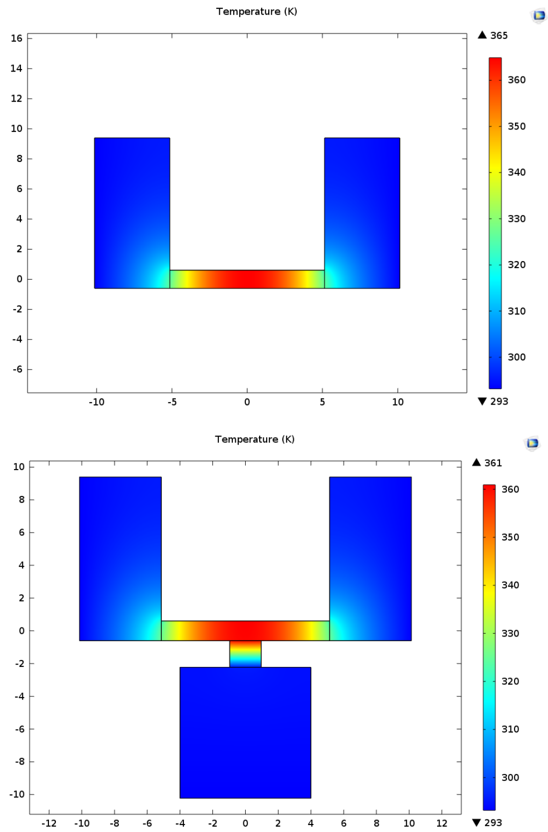

Fig. 3 Temperature distribution of T-type sensor

Figure 3 shows the temperature distribution of T-type sensor with and without graphene ribbon. If the graphene ribbon is attached on the sensor, the average temperature of sensor is reduced because part of heat is conducted to the heat sink through the graphene. By measuring the temperature difference of sensor with and without graphene, the thermal conductivity of graphene can be calculated based on the 2D thermal analysis result.

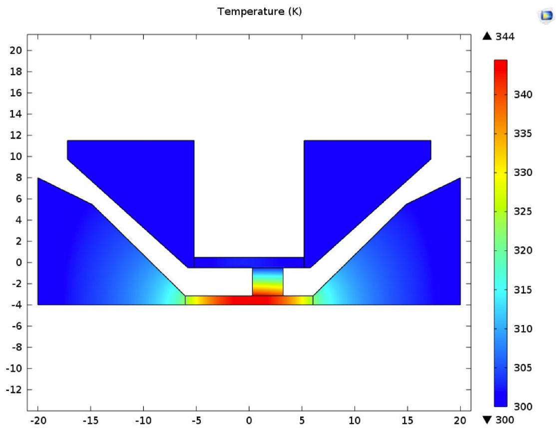

Fig. 4 Temperature distribution of H-type sensor

Figure 4 shows the temperature distribution of H-type sensor, where a graphene ribbon bridges between two suspended sensors. In this case, the temperature changes of two sensors can be measured simultaneously. Since the graphene ribbon is the only heat conduction channel between two sensor, the thermal conductivity of graphene is directly related to the temperature difference between two sensors. By comparing the measured temperature difference between two sensors with the 2D thermal analysis result, the thermal conductivity of graphene can be determined.

In this project, we have measured the thermal conductivity of graphene by using both T-type and H-type methods. The results agree well with each other, over 2000 W/mK. It proves the high accuracy and repeatability of our method.

4．研究成果

We have measured thermal conductivities of graphene samples with different defects, sizes. The result is shown in Fig. 5. Some main conclusions are shown here.

(1) For the suspended pristine graphene without hole defect, the thermal conductivity is the highest, over 2000 W/mK at room temperature. It also agrees well with the other data from Raman measurement [2].

(2) If there are nanohole defects on graphene, the thermal conductivity will be significantly reduced by about 50%. In this case, the phonon defect scattering is important and limit the propagating phonon modes.

(3) The thermal conductivity of graphene depends on its width. For the wider graphene, the thermal conductivity is larger. It means that the phonon edge scattering is also important for the micrometer wider samples. For the narrower graphene ribbon, the edge scattering is stronger and the thermal conductivity is relatively smaller. This is also a direct evidence to show that the

phonon mean free path in graphene is quite long, over several micrometers.

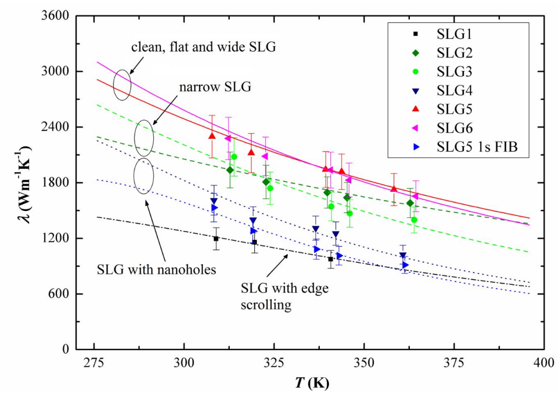

Fig. 5 Thermal conductivity of suspended graphene

More importantly, we have confirmed that the interfacial effect plays an important role in determining the thermal conductivity of graphene. Fig. 6 shows the thermal conductivity of supported graphene measured by using the similar MEMS device method in the literature [3].

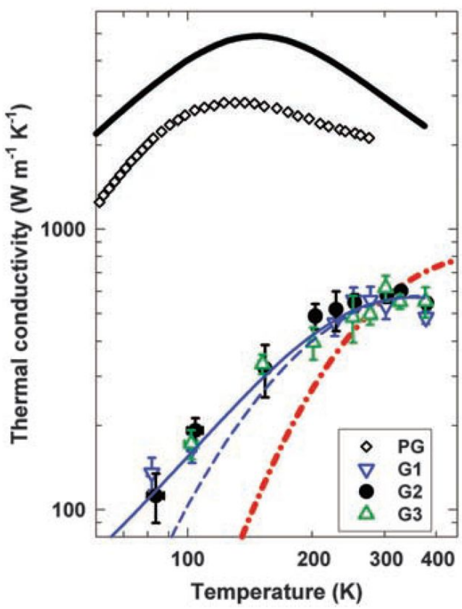

Fig. 6 Thermal conductivity of supported graphene on SiO_2 [3]

The measured thermal conductivity of supported graphene on SiO_2 is about 600 W/mK at room temperature, much smaller than the value of suspended graphene. Because both thermal conductivities of suspended and supported graphene were measured by using MEMS device method, the measurement uncertainty and sample quality were very close to each other. The measurement uncertainty is about 5% by using MEMS sensor. As a result, the measurement error cannot be the reason for such large difference in the thermal conductivities of suspended and supported graphene samples. The interfacial effect is the only reasonable mechanism to explain this difference. The interfacial effect can decrease the thermal conductivity of monolayer graphene by 70% at room temperature. This difference is mainly due to the strong phonon substrate scattering. For the supported graphene, the lattice vibration in the thickness direction is limited by the interaction with substrate, then the in-plane phonon mean free path is significantly reduced and the thermal conductivity is reduced as well.

Our new findings provide the direct and solid experimental evidence for the strong interfacial effect of graphene in limiting its thermal conductivity. It provides valuable experimental data for the future design of graphene heat spreaders.

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５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

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