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ロックイン探針増強非定常ラマン法の確立と２次元熱伝導マッピング

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Lock-in tip-enhanced transient Raman method for 2D heat conduction mapping

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ナノ材料の熱物性データは数 10%といった大きな誤差を含む場合が多く、欠陥と界面の影響についても調べる手法が限られている。本研究では、高い時空間分解能を有する熱物性計測法の開発を進めている。まず、走査型熱顕微鏡に基づいて 2 次元材料の熱物性分布を高精度にマッピングする手法を開発した。更に、高い時間分解能を有する非定常ラマン分光法を用いてグラフェンフォームの熱拡散率を測定し、ロックイン技術によってラマン分光法の計測精度も改善して進めている。

The measured thermophysical properties of nanomaterials often exhibit large uncertainties and there are very limited methods to experimentally study the thermal transport at the defects and interfaces. In this study, we develop methods to measure the thermophysical properties with high temporal and spatial resolutions. First, we developed an approach to map the distribution of thermophysical properties in 2D materials with a high spatial resolution based on the scanning thermal microscope. Second, we measured the thermal diffusivity of the graphene foam using the transient Raman method with a high temporal resolution and utilized the lock-in technique to improve the accuracy of Raman thermometry.

1. 研究内容

1.1 Thermophysical property mapping along a graphene ribbon using scanning thermal microscopy

In this study, we set up the scanning thermal microscopy (SThM) probe to the atomic force microscope (AFM) and realized temperature mapping with a spatial resolution as high as 50 nm. Then we used SThM to measure the temperature distribution along a defected graphene ribbon under Joule heating, as illustrated in Fig. 1, and determined the interfacial thermal conductance between graphene and the underneath SiO2 with a high spatial resolution.

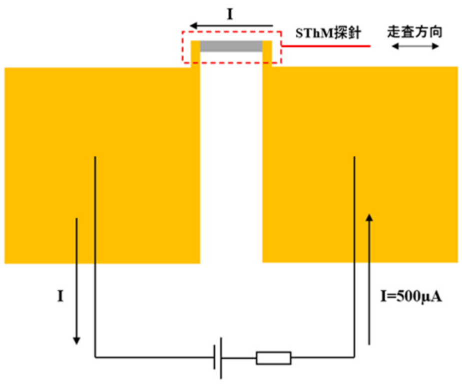

Figure 1. Schematic for the interfacial thermal conductance mapping along a graphene ribbon

The graphene ribbon sample was fabricated by a series of MEMS processes including wet transfer of CVD-grown monolayer graphene onto the SiO_2/Si wafer, electron beam lithography for the patterning, physical vapor deposition of the metallic electrodes, as well as wire bonding. We confirmed the high quality of the graphene sample with Raman spectroscopy and measured the temperature dependence of the G band and 2D band of the graphene sample. We measured that both the Raman G band and 2D band shifts decrease with increasing temperature at a slope of -0.0389 cm^{-1}/K and -0.0394 cm^{-1}/K, respectively.

We optimized the scanning conditions for the cantilever probes of the AFM and SThM so that we can introduce defects into the graphene ribbon in a controllable way. The spring constant of the probe in our experiments was 9.9 N/m. When we applied an operation potential of 0.1 V and a scan speed of 12 μm/s, there existed no observable defects that are induced by the probe on the graphene sample. However, when we applied a high operation voltage of 1 V and a high scan speed of 40μm/s～200μm/s, we can introduce micrometer scale defects on the graphene sample. Furthermore, we fulfilled line scan with the AFM probe and successfully introduced line defects in the graphene sample.

We heated the graphene sample with direct current in two modes and measured the temperature distribution along the graphene ribbon. In the first mode, we drove current in a thin metallic (Au) film near the graphene sample and mapped the temperature distribution on both graphene and SiO_2 areas. When the heating current in the thin Au film was 70 mA, the temperature on the graphene area was 1.37 K lower than that on the SiO_2 area, which indicated the cooling effect of graphene. In the second mode, we drove current in the graphene ribbon and investigated its temperature distribution under Joule self-heating. We measured the electrical conductivity of the monolayer graphene to be as high as 3.52×10^5 S/m, indicating high quality of the sample. We observed local hot spots at the vicinity of defects and estimated the interfacial thermal conductance between monolayer graphene and SiO_2 to be 24.48MW/m^2·K using the Joule heating power and the measured graphene temperature.

1.2 Thermal diffusivity measurement of graphene foam using the transient Raman method

In the conventional steady-state Raman optothermal method, continuous laser is used to heat the sample, while the local temperature of the sample is detected based on the temperature dependence of the Raman spectrum of the sample in a non-contact manner. Then the thermal conductivity of the sample can be derived from the relationship between the absorbed laser power, i.e. the heat flux, and the Raman-measured temperature. However, in this steady-state Raman method, the laser absorptance is difficult to be accurately determined, especially for micoscale and nanoscale samples, thus causing a large uncertainty.

In this study, we measured the thermal diffusivity of CVD grown graphene foam using the transient Raman method. The graphene foam was suspended between two Si wafers that served as heat sinks. We used pulsed laser to heat the sample and measured the transient temperature increase from the temperature dependence of the Raman shift of the graphene foam. We observed a strong G band and a weak D band in the Raman spectrum. which indicates high quality of the sample. As shown in Fig. 2, by changing the laser pulse duration, we measured the change of the G-band Raman shift that reflects the temperature evolution. From this temperature change as a function of the pulse duration, we can extract the thermal diffusivity without the need of knowing the absorptance of the heating laser. Specifically, for this graphene foam sample, the laser spot size is much larger than the sample size and the heating laser can be regarded as a point heat source. We performed finite-element simulations for the transient temperature evolution of the graphene foam under point heat source and established the relationship between the normalized temperature rise and the thermal diffusivity. Then, by comparing the simulation results with our experimental data, we can determine the thermal diffusivity of the sample. We can further determine the thermal conductivity with the specific heat and density. In this way, we can eliminate the uncertainty of the laser absorptance and measure the thermal property with a high accuracy. We successfully measured the effective thermal conductivity of this 3D porous graphene foam to be 5.4W/mK, which is about 1/500 of that of monolayer graphene.

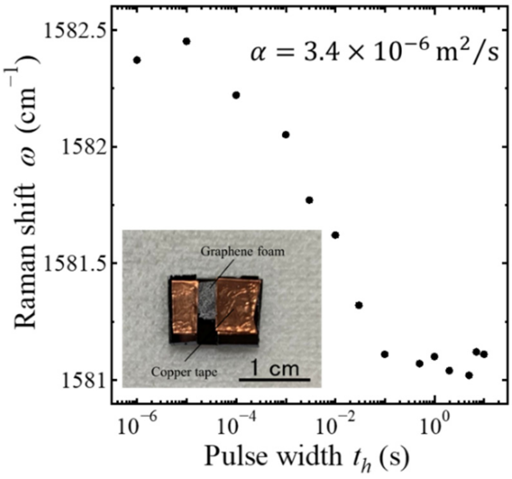

Figure 2. Thermal diffusivity measurement of graphene foam

1.3 Development of the lock-in Raman method

The Raman based temperature measurement suffers from the relatively low temperature resolution, typically about 5 K. In this study, we propose a lock-in technique to improve the temperature measurement accuracy. We use sinewave modulated current to heat the sample and pick up the change in the Raman shift that is at the same frequency of the heating power. In this way, the noises at other frequencies can be eliminated and we can improve the temperature resolution to about 0.5 K. Using this method, we measured the thermal conductivity distribution in a carbon fiber network with a high resolution.

2. 発表（研究成果の発表）

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