

Application of Graphene Towards Thermal Management

Takamoto Yokosawa, Tomohiro Matsui

[Summary]

A novel thermal properties different from the classical understanding are expected when wave nature of phonon, a quasi-particle of lattice-vibration which is responsible for the heat conduction, becomes significant by miniaturizing devices relative to the mean-free-path of phonons. In this study, unconventional thermal conductivity, which increases with decreasing the nanoribbon width, were discovered by fabricating graphene with long mean-free-paths into nanoscale mesh structures with atomically ordered zigzag edges. The maximum thermal conductivity of the mesh structure is equivalent to or greater than the highest thermal conductivity reported for carbon nanotubes, and is nearly an order of magnitude larger than the heat dissipation sheets characterized by high thermal conductivity. Moreover, the thermal conductivity can be varied by a factor of nearly 8 simply by changing the nanoribbon width. Since these features are obtained regardless of a substrate, this feature could be applied to heat dissipation and rectification sheets.

1 Introduction

We, human beings, have acquired techniques for controlling electricity and handling light. Recently, the importance of technologies for handling and controlling heat, such as predicting temperature, cooling materials, and dissipating heat efficiently, is increasing. The size ranges widely from the μm scale of electronic devices to the cm scale of devices like smartphones, and even to the meter scale of automobiles and factories. For example, in electronic devices, not only the dissipation of heat generated by electronic components, but also the heat-dissipation pathways must be designed carefully to prevent heat adversely affecting adjacent components. In fact, heat generation by electronic devices has become a barrier to integration of components and performance improvement. Such heat control — thermal management — technologies, can be essential for a future IoT and energy-efficient society.

Graphene, which is a one-atom-thick carbon film, is the focus of thermal management research, too, because it is extremely thin, lightweight, transparent, mechanically strong yet flexible, and has excellent electrical and thermal conductivity. As shown in Table 1 listing the thermal conductivity of major materials, graphene has a thermal conductivity of nearly an order of magnitude greater than common metals, such as copper.

As quasi-particles called electrons and photons conduct electricity and light, heat is conducted by quasi-particles

called lattice vibrations (phonons). The average distance these phonons travel without colliding with each other is called the mean-free-path, and the mean-free-path is important for evaluating conduction properties. When the system size is longer than the mean-free-path (or when the mean-free-path is short compared to the system size), the quasi-particles collide with each other before they collide with the system boundary. In this case, the ‘particle’ nature of the quasi-particles becomes dominant, and conduction becomes diffusive. In contrast, in nanoscale devices or at low temperatures where the mean-free-path is long, quasi-particles are scattered at the system boundaries before colliding with each other. In this case, conduction becomes ballistic, and a wave-like nature emerges, in which information intrinsic to quasi-particles, such as the phase, is preserved. Generally, diffusive conduction, expressed by the Boltzmann equation, dominates, and ballistic conduction is only possible in nanostructures at ultra-low temperatures. However, since the mean-free-path of graphene is long due to its high crystallinity, unique thermal conduction properties, that cannot be obtained with ordinary materials, can be achieved even at room temperature.

Table 1 Thermal Conductivity of Major Materials

Material	Thermal Conductivity (W/(m · K))
Graphene	3000 – 5300 ¹²⁾
Carbon nano tubes	3000 – 3500 ^{3), 4)}
Diamond	1000 – 2200 ¹⁾
Graphite	72 – 2100 ⁵⁾
Copper	403 ⁶⁾
Si	168 ⁶⁾
SiO ₂	1.4 ⁶⁾
Water	0.561 ⁶⁾
Air	0.024 ⁶⁾

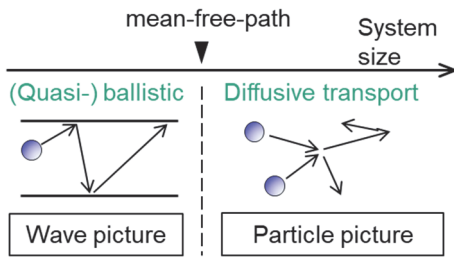


Figure 1 Schematics of ballistic and diffusive transports.

On the other hand, considering the device structure, new functions can be achieved by designing artificial nano- or micro-meter scale structures. It is called “meta-materials”, which enables characteristics that were previously thought impossible with conventional materials, such as negative refractive indices and invisibility cloaks. In such way, novel properties can be expected for graphene by nano-structuring and by arranging nano-structures periodically.

This paper introduces the thermal conductivity of graphene which is nano-fabricated into mesh and ribbon structures using our unique hydrogen plasma etching technique. General understandings of the thermal conductivity were described in section 1. Section 2 introduces previous research on thermal conductivity of microfabricated graphene, and section 3 introduces samples and measurement methods in this study, and discusses the measured results.

2 Thermal Conductivity of Microfabricated Graphene

Thermal conductivity is generally decreased by nano-structuring, since phonon scattering at the edges is increased, and this is also the case for graphene. For example, it is observed for an array of nanoscale graphene ribbons (Graphene Nano Ribbons: GNR) with widths (W) of 45 to 130

nm that the thermal conductivity decreases by decreasing W ⁷⁾. Here, GNR is fabricated by oxygen plasma etching of graphene obtained by exfoliating graphite on SiO₂ substrates (exfoliated graphene). This research measured the thermal conductivity by applying heat from a heater to one end of the GNR and measuring the temperature change at the opposite end. Since the GNRs are supported by SiO₂ substrate in this study, the thermal conductivity is determined by the thermal conduction with and without GNRs.

Smaller thermal conductivity has also been reported⁸⁾ as the neck width becomes narrower in graphene meshes with circular holes, where the average distance between holes (neck width) is about 8 to 21 nm. Here, graphene itself was obtained by chemical vapor deposition (CVD) method. The meshed graphene in this research were fabricated by reactive ion etching (RIE) using a polymer mask, and then transferred to a SiN membrane with holes to prepare a meshed graphene suspended from the substrate. Thermal conductivity was determined by Raman spectroscopy.

Thermal rectification, in which heat flows only in the desired direction, can be achieved by controlling thermal conductivity with nanostructured graphene. Asymmetric thermal conduction has been reported⁹⁾ for suspended graphene where a region with 5 to 6 nm diameter holes is arranged in a square lattice with 30 nm spacing adjacent to a region without holes. It was observed that the thermal conductivity is higher when heat flows from a region with holes to a region without holes than in the reverse direction. This is thought to occur because high-energy phonons localize in the region with holes, resulting in an asymmetric temperature distribution. Applications for thermal rectification devices (thermal diodes) allowing heat to flow only in one direction can be expected using this effect.

3 Thermal Conductivity of Graphene with Zig-Zag Edges

3.1 Sample Preparation

We have developed a technique to process graphene at the atomic scale using hydrogen plasma etching¹⁰⁾. Since the edges of the processed graphene have atomically-ordered zigzag structures^{11, 12)} terminated with single hydrogen atoms¹³⁾, ideal zigzag edges that maintain graphene’s sp² bonding all the way to the edge can be obtained with this technique. This

contrasts with edges obtained by conventional processing methods such as oxygen plasma etching and RIE that have random structures at the atomic scale and, in some cases, may be disordered in an amorphous state.

Hydrogen plasma etching forms nanoscale hexagonal holes (nanopits) in graphene, centered around defects that serve as seeds for etching. These hexagonal nanopits can be used as basic elements for processing graphene. If the defects, seeds for nanopits, are processed into an elliptical shape, elongated hexagonal nanopits are formed, and GNRs can be obtained between the hexagonal nanopits arranged in parallel. Unlike previous studies⁷⁾, the edges of these GNRs are ordered atomically in a zigzag pattern, so they are called as zigzag GNRs (zGNRs). Additionally, if hexagonal nanopits are arranged in a triangular lattice, a graphene mesh structure can be created. This could be considered as an “antidot lattice” focusing on the periodic arrangement of holes, or it could also be considered as a “zGNR network” focusing on how the zGNRs are connected in a mesh-like pattern. In this article, this structure is described as a zigzag graphene nanomesh (zGNM). By etching away the substrate after attaching electrodes to the fabricated graphene, a suspended structure bridged between the electrodes are obtained. Since graphene is extremely thin, it is susceptible to influences such as substrate roughness and charge transfer from the substrate. However, these effects can be eliminated by creating a suspended structure.

3.2 Thermal Conductivity Measurement by Raman Spectroscopy

There are two general methods for measuring thermal conductivity: the steady-state method and the transient method. The steady-state method applies a thermal gradient to a device by setting different temperatures at both ends of the device, and thermal conductivity is determined by measuring the temperature at various points within the device. In contrast, the transient method applies a known amount of heat to the device and the thermal conductivity is determined from the resulting temperature change of the device. This study measured the thermal conductivity of graphene devices using the transient method known as opto-thermal Raman measurement employing Raman spectroscopy. In this method, the laser light for Raman spectroscopy serves as the heat source, and temperature

changes are measured using shifts in the Raman spectrum. In case of graphene, G, 2D, and D bands appear in the Raman spectrum, and the G and 2D bands are known to red-shift with increasing temperature¹⁴⁾⁻¹⁶⁾. Among these two G and 2D bands, the 2D band arises from second-order phonon scattering and changes its shape depending on the number of graphene layers, while the shape of the G band originating from in-plane vibrations of graphene honeycomb lattice does not depend on the number of graphene layers. Therefore, the temperature of graphene was estimated from the shift of the G band in this study.

The G-band shift $\Delta\omega_G$ (cm^{-1}) is reported^{14), 15), 17)} to be proportional to the graphene temperature change ΔT as shown in the Eq. (1).

$$\Delta\omega_G = \chi\Delta T \quad (\chi \cong -1.6 \times 10^{-2} \text{ cm}^{-1}/\text{K}) \quad (1)$$

The amount of heat absorbed by graphene P_{abs} (W) is expressed by Eq. (2) as a function of the excitation laser power P (W) irradiated to graphene, the absorptivity of graphene α ($\sim 2.3\%$ ¹⁸⁾), the number of layers N (thickness $t \cong N \times 0.335 \text{ nm}$), and the ratio of the area occupied by graphene inside the laser spot S .

$$P_{\text{abs}} = P(1 - \exp(-\alpha N)) S \quad (2)$$

Figure 2 shows the G-band peaks measured for a zGNM at different laser powers. As the power increases, the temperature of graphene rises, causing the G-band to shift toward the lower frequency (longer wavelength).

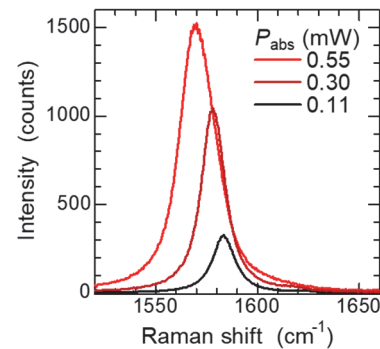


Figure 2 Changes of G-band peak when varying laser power irradiating graphene. As the amount of heat absorbed by graphene increases, the signal intensity becomes larger, while the peak center shifts toward the lower frequency.

Since the thermal conductance K (W/K) is the coefficient of temperature change when heat is loaded to a substance, that is

$$P_{\text{abs}} = K\Delta T. \quad (3)$$

K can be described with P_{abs} and $\Delta\omega_G$ as

$$K = \chi \left(\frac{\partial \Delta \omega_G}{\partial P_{\text{abs}}} \right)^{-1} \quad (4)$$

In this study, zGNM, graphene processed into a mesh pattern (Figure 3(a)), and zGNR, graphene processed into a ribbon pattern (Figure 3(b)), were used as samples. We used exfoliated graphene with 2 to 10 layers thick and varied the width of the nanoribbon (W) from 20 to 160 nm. The arrangement periodicity of hexagonal nanopits is 350 to 540 nm for zGNM. Electrodes were attached to the zGNM and zGNR devices as shown in Figure 3, and the excitation laser irradiated the central part of a device. As a result, the electrodes act as a heat bath at room temperature, and the heat is expected to flow from the central part of the device toward the electrodes. Equation (5) was used to determine the thermal conductivity κ (W/m·K) from K taking into account the size of the device.

$$\kappa = \frac{L_{\text{eff}}/2}{tW} K \quad (5)$$

Here, L_{eff} is the length of the thermal conduction path indicated by the red lines in Figure 3, and W is the width of the nanoribbons making up the ribbon or mesh. Although a quasi-one-dimensional thermal conduction path was assumed for mesh-structured devices, heat can also flow parallel to the electrodes, in reality. It possibly results in overestimation of κ . Additionally, among two types of devices used in this study: suspended (floating above substrate) and supported (held on substrate), it should be noted that the effects of the substrate are included in κ of supported devices.

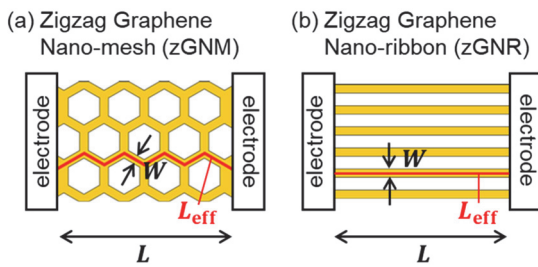


Figure 3 Schematics of (a) zGNM and (b) zGNR devices with electrodes attached. A quasi-one-dimensional path indicated by the red line was used to calculate κ for zGNM.

To prevent degrading the graphene device by continuous irradiation of the excitation laser, the laser irradiation time should be as short as possible. However, this results in a poor spectrum signal-to-noise (S/N) ratio. To overcome these contrary effects, short time (~ 0.02 s) measurement was repeated. On the other hand, the laser focus becomes

misaligned due to thermal drift as measurement progressed. Therefore, each spectrum was obtained by changing the height of the objective lens, and the G-band wave number when the laser was focused at the sample position was extracted. Figure 4 shows the dependence of the G-band wavenumber (ω_G) and intensity (I_G) on the objective lens height (z) for each measurement. The results show how z , where ω_G becomes minimum and I_G becomes maximum, changes gradually as measurement was repeated. The measured minimum values of ω_G obtained in this way were averaged.

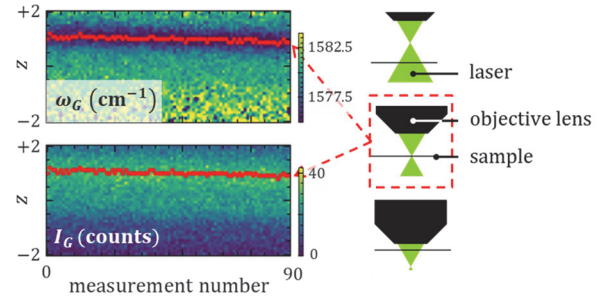


Figure 4 Changes in G-band wavenumber (ω_G) and intensity (I_G) at each measurement while repeatedly scanning lens height (z), and schematic of relationship between spread of laser irradiated through objective lens and sample position. The objective length height, z , where ω_G becomes minimum (and I_G becomes maximum) for each measurement is indicated by a red dot. The laser is focused at this height.

Figure 5 shows the G-band shift ($\Delta \omega_G$) normalized by device dimensions ($(2tW/L_{\text{eff}})\Delta \omega_G$) relative to the heat absorbed by graphene (P_{abs}) for devices with various ribbon widths (W). It shows that the G-band shifts largely as P_{abs} increases. According to Eqs. (4) and (5), the reciprocal of this slope corresponds to the thermal conductivity κ . Contrary to the classical picture, the slope of the graph becomes more gradual as W becomes narrower, meaning that κ is increasing.

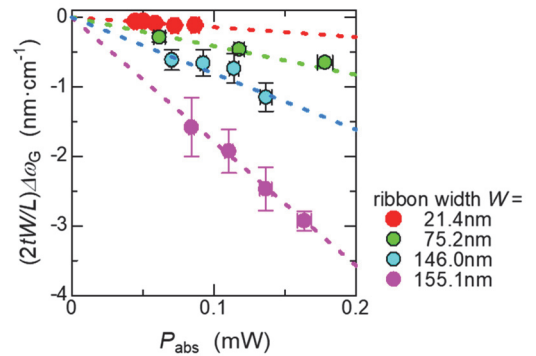


Figure 5 P_{abs} dependence of G-band shift normalized by device dimensions for zGNMs with different ribbon widths (W). Linear fits are shown as dotted lines.

3.3 Thermal Conductivity of Suspended Sample

Figure 6 shows the dependence of thermal conductivity (κ) on ribbon width (W) for (a) suspended zGNM and (b) suspended zGNR. The graphene thickness (t) dependence of κ suggests that, κ does not depend on t for 4 or fewer graphene layers (thin) and 5 or more graphene layers (thick). Therefore, in Figure 6, samples with 4 or fewer layers are shown in blue, and samples with 5 to 10 layers are shown in red. Only the κ for zGNRs with 5 to 10 layers is shown in red, since zGNRs with 4 or fewer layers could not be created. Surprisingly, κ is found to be inversely proportional to W for suspended zGNMs (Figure 6(a)) with 4 or fewer layers (thin). In addition, for 5 to 10-layer (thick) zGNMs, κ remains nearly constant for W down to ~ 30 nm. This behavior contradicts the classical picture where κ decreases as the structure becomes smaller due to increased phonon scattering.

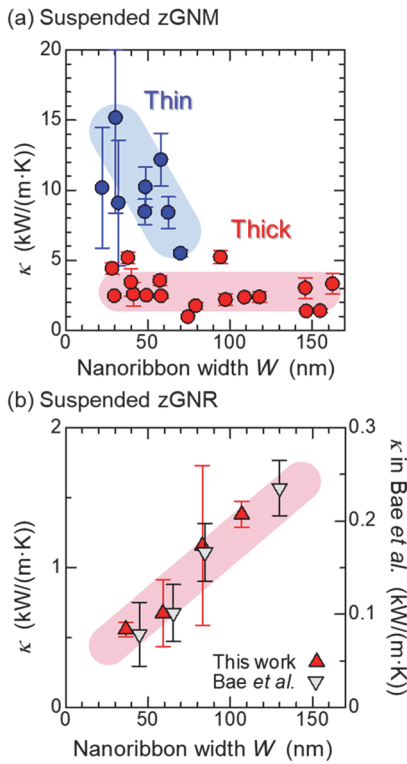


Figure 6 Dependence of thermal conductivity (κ) on ribbon width (W) for (a) suspended zGNM (●) and (b) suspended zGNR (▲/▽). Thin samples with 4 or fewer layers are shown in blue, and thick samples with 5 to 10 layers are shown in red. ▲ in (b) represents the results of this measurement (left axis), and ▽ represents the results of previous research⁷⁾ (right axis).

On the other hand, for suspended zGNR, κ decreases as W becomes narrower, similar to previous research. As superimposed the results of previous research⁷⁾ in Figure

6(b), our result shows the similar dependence of κ on W . Accordingly, it can be considered that the inverse proportionality of κ to W in suspended zGNM is due not to the zigzag edges but to the mesh structure. Although the detailed examination of this mechanism is the subject of future research, it is possible that κ is enhanced due to the interference of phonons in the nano-scale mesh structure as a result of the wave nature of phonons becoming non-negligible. In fact, enhancement of the thermal conductance as the spacing between circle holes decreases (phononic boost) has been calculated for an 80 nm silicon thin film with periodically placed circular holes (phononic crystal) at ultra-low temperature of 1K¹⁹⁾. This is because of the increased phonon density caused by phonon interference.

Although the dependence of κ on W for suspended zGNRs is similar to previous study, the value of κ is 6 to 7 times larger than the prior one. Compared to this study, the GNRs in previous study were supported on SiO₂ substrates²⁰⁾, and were made from single-layer graphene²¹⁾, while this study used graphene with 5 to 10 layers thick. Nevertheless, even after taking these differences into account, the zGNRs fabricated in this study still show approximately four times larger values of κ than GNRs from previous study. This suggests that the atomically ordered zigzag edges of zGNRs fabricated in this study increase the κ compared to previous devices with random or amorphous edges. In fact, several theoretical studies^{22), 23)} have proposed that GNRs terminated with zigzag edges (zGNRs) show larger κ than GNRs terminated with armchair edges (aGNRs). On the other hand, since κ can be overestimated for zGNMs as discussed before, the fact that zGNMs show several times larger κ than zGNRs might be due to such mathematical effects.

3.4 Thermal Conductivity of Supported Sample

Figure 7 shows the dependence of κ on nanoribbon width (W) for (a) supported zGNM and (b) supported zGNR. Since the κ is calculated only from the device dimensions and the effect of the substrate is not considered, the κ here are nominal values. Since the κ of supported samples do not depend on the graphene thickness (t) unlike suspended samples, the data for all samples with 2 to 10 layers thick are shown without categorizing. Here, non-classical behavior where κ increases as W decreases are observed for both supported zGNMs and zGNRs.

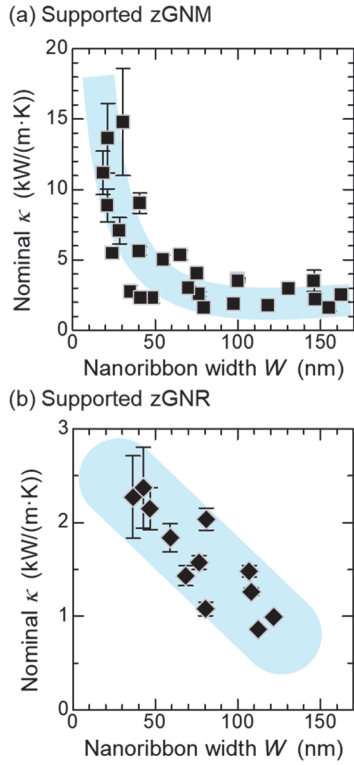


Figure 7 Dependence of thermal conductivity (κ) on nanoribbon width (W) for (a) Supported zGNM and (b) Supported zGNR.

Considering the results of suspended devices, the fact that the κ does not suppressed in supported samples despite nanostructuring can be attributed to the substrate effects rather than device structure or zigzag edge effects. This suggests that, despite the SiO_2 being an electrical insulator and poor thermal conductor, heat flow to the SiO_2 substrate cannot be ignored, and the substrate effect becomes more significant as device size decreases. This can be explained by three-dimensional (3D) heat spreading from the device to the substrate²⁴⁾. As shown in Figure 8, heat from the device surface flows perpendicular to the surface into the substrate. However, it flows radially at the device edges. While heat flow in the perpendicular direction is dominant when the device is large, the effect of 3D flow into the substrate becomes more significant as the device becomes smaller, increasing the nominal κ of a device.

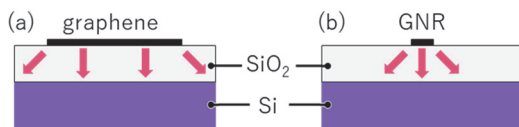


Figure 8 Schematics of heat dissipation from (a) graphene and (b) GNR to substrate.

4 Conclusions

Similar to electrical conductivity, thermal conductivity (κ) generally decreases as devices become smaller. However, under conditions where the wave nature of quasi-particles responsible for heat conduction becomes significant, κ can possibly increase with device miniaturization. This study demonstrated that the thermal conductivity (κ) increases as nanoribbon width (W) decreases by processing graphene with high crystallinity and long mean-free-path processed into a mesh structure with atomically ordered zigzag edges. The increase in κ becomes significant at W of <100 nm and reaches $\sim 15,000$ W/(m·K) at W of ~ 30 nm. This is the world's first experimental demonstration that κ increases due to the wave nature of the lattice vibration and its interference.

Graphene is expected to be used as a key material for heat dissipation and thermal control in high-frequency circuits, power-supply circuits, high-sensitivity sensors, etc., due to its higher thermal conductivity (κ) compared to other materials. It is useful from an application perspective that its κ can be further enhanced by fabricating it into a mesh structure as demonstrated here. For carbon nanotubes (CNTs), which are attracting attention as heat-dissipation materials due to high κ , the ideal value of κ is reported²⁵⁾ to be 6,600 W/(m·K). There are also reports²⁶⁾ of high thermal conductivity reaching 13,300 W/(m·K) by employing specialized sample preparation techniques. Although κ for suspended zGNMs can be overestimated when it is calculated from thermal conductance (K), it is worth noting that we obtained a κ that is equivalent to or higher than that of CNTs with high thermal conductivity. Commercially, heat-dissipation components based on graphene with high thermal conductivity reaching 1,800 W/(m·K) have been reported^{27), 28)}, but the κ value of zGNMs fabricated in this study exceeds that by almost an order of magnitude, suggesting promising future applications.

It is also an advantage of the zGNM fabricated in this study that the value of κ can be controlled by a factor of about 8 simply by changing the W . This feature enables to design graphene sheets with desired κ depending on the applications.

Another important discovery is that this unconventional behaviour can be obtained in the presence of a substrate. It can overcome the problem of single layer graphene sheets

curling up due to the Mermin-Wagner theorem. Additionally, in general, multi-layer graphene is easier to handle than single layer graphene. The fact that multi-layer graphene supported on substrate can have a high value of κ that is inversely proportional to W strongly suggests possibilities for practical applications.

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Authors



Takamoto Yokosawa
MATSUI Laboratory
Advanced Research Laboratory



Tomohiro Matsui
MATSUI Laboratory
Advanced Research Laboratory

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