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Thermoelectric measurements of nanomaterials by nanodiamond quantum thermometry

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In this study, the Seebeck coefficient of a single-walled carbon nanotube (SWCNT) was evaluated using a nitrogen vacancy center in nanodiamonds as a thermometer. A temperature gradient was established across the SWCNT, and the temperatures of the nanodiamonds on the electrodes, along with the electromotive force between these electrodes, were measured. The Seebeck coefficient for a metallic SWCNT was determined to be $14.0 \pm 1.1 \,\mu$ V K⁻¹, which is consistent with results reported in previous studies. This methodology offers a promising approach for evaluating the thermoelectric properties of various nanomaterials. © 2024 The Author(s). Published on behalf of The Japan Society of Applied Physics by IOP Publishing Ltd

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hermoelectric power is an essential green energy source, emphasizing the need to enhance the performance of thermoelectric materials. Theoretical studies by Hicks and Dresselhaus¹⁾ in 1993 demonstrated the potential for increased thermoelectric efficiency in onedimensional (1D) materials, sparking a surge of research into the measurement of 1D materials. However, measuring the Seebeck coefficient of 1D nano-sized materials presents challenges related to handling and temperature measurement.

One proposed method involves measuring temperatures at both ends of the 1D material by using the temperaturedependent resistance of micrometer-scale metal electrodes positioned at each end.^{2–4)} This method can accurately determine the average temperature of the entire electrode, with an error margin of much less than 0.1 °C. However, the electrodes must be sufficiently long and narrow to accurately estimate their temperature-dependent resistance values. Ensuring uniform heating along the entire length of the electrode is challenging. Moreover, the four-terminal method necessitates numerous electrode configurations, increasing the complexity. Therefore, a direct method for determining the temperature at both ends of 1D nanomaterials is required.

Another approach involves synthesizing a 1D material of considerable length⁵⁾ and measuring the temperature difference between both ends using a conventional large thermometer. However, this method necessitates advanced techniques to fabricate materials with narrow diameters and significant lengths. For this method to be applicable, the 1D material must be sufficiently long to allow measurement, making it challenging to investigate micrometer-scale effects on the 1D length-dependent electrothermal characteristics.

Furthermore, numerous studies have focused on measuring bulk 1D materials (aggregates of materials) to estimate their thermoelectric properties. For instance, single-walled carbon nanotubes (SWCNTs) have been characterized using chirality separation techniques. Measurements have examined gate dependence,⁵⁾ temperature dependence,⁶⁾ and chirality dependence⁷⁾ with significant findings reported⁸⁾ and theoretically predicted.^{9,10)} However, these studies indicated that impurities and bundles in aggregated materials can significantly alter their thermoelectric properties. Owing to the challenges in achieving 100% purity, evaluating pure materials is difficult when using aggregated samples. Therefore, measuring individual SWCNTs is necessary to accurately determine these properties. Efforts have been made to determine temperatures using Raman and photoluminescence spectroscopy on individual SWCNTs,^{11,12} however, a precise methodology has not been established, and issues related to laser-induced damage persist.

A major challenge in measuring the temperature-related properties of nanoscale materials is the unsuitability of conventional thermometers. To address this issue, we measured the thermoelectric properties of nanodiamonds using their nitrogen-vacancy (NV) centers, which have shown promise in accurately measuring nano-sized temperature characteristics. NV centers have garnered significant attention in recent years as quantum sensors capable of measuring temperature,¹³⁻¹⁶⁾ magnetic fields,¹⁷⁾ and electric fields.¹⁸⁾ The size of the thermometer is determined by the size of the nanodiamond, making it ideal for measuring nanodevices. Temperature is determined by the center frequency shift of the optically detected magnetic resonance (ODMR) of NV defect centers, primarily resulting from thermal lattice expansion. Research on in vivo temperature measurement has been actively conducted in recent years, focusing on the accuracy of measurements. However, practical applications, such as temperature sensors and their utilization in research to elucidate physical phenomena, are still in their infancy. This study aimed to develop and demonstrate a method for measuring the Seebeck coefficient of nanomaterials, particularly SWCNTs, using a diamond NV quantum sensor near RT. SWCNTs have garnered significant attention due to their high performance, flexibility, and lightweight nature as 1D materials. The Seebeck coefficient was estimated from the temperature difference measured by the nanodiamond and the voltage difference between the electrodes at each end of the SWCNT.

The sample fabrication process involved dispersing SWCNTs synthesized using the eDIPS method (EC1.5, Meijo Nano Carbon) in an aqueous solution of the surfactant





Fig. 1. (a) Optical microscopy image of the sample captured using a $40 \times$ lens with design drawing. The green line indicates the location of SWCNTs identified prior to the design. As local heaters, three electrodes were placed near the SWCNTs. (b) Confocal photoluminescence image of the sample. (c) Schematic of the experimental setup for the optical temperature measurement and microwave circuit. The measured nanodiamond was labeled NDH (hot side) and NDC (cold side). (a) and (b) were also obtained by this microscope. (d) A four-point ODMR measurement scheme determined the center frequency (D(T)), which is temperature-dependent. I_1 to I_4 represent the intensity measurements at four frequencies. (e) Four-point measurements. 532: green laser. MW1 to MW4: four frequencies, I_1 to I_4 were measured with the same DAQ counter and sorted into arrays.

sodium cholate using a homogenizer. The solution was then ultracentrifuged to collect supernatants containing isolated SWCNTs. Subsequently, the solution was diluted with water, and the SWCNTs were dispersed onto a Si/SiO_2 substrate with a SiO_2 thickness of 200 nm.

The selected SWCNT had a diameter of approximately 1 nm, which is sufficiently small to ensure that it was considered an isolated SWCNT rather than a bundle. Electrodes and heaters were designed based on the positions of the SWCNTs. The distance between the two electrodes was $2.2 \,\mu$ m, with a width of $0.5 \,\mu$ m. Local heaters were positioned near the hot electrode. Using electron-beam lithography, Pd (90 nm) which was known for its low contact resistance with SWCNTs¹⁹⁾ were formed. Prior to the lift-off process, nanodiamonds were dispersed on the substrate by spin coating, with multiple spin-coating steps to achieve the desired density. Nanodiamonds containing over 1000 NV centers per particle (brFND-100, FND Biotech) were utilized and were placed exclusively on the electrodes to facilitate easy identification of their positions.

Optical microscopy images of the sample, along with a design schematic, are displayed in Fig. 1(a). A hot electrode was installed at one end of the SWCNT and a cold electrode at the other, with local heaters adjacent to the hot electrode. The location of the SWCNT is delineated by a green line running between the hot and cold electrodes. The scanning confocal microscopy photoluminescence image in Fig. 1(b) shows the exclusive placement of nanodiamonds on the electrodes. Nanodiamonds positioned nearest to the SWCNT root were meticulously selected to measure the temperature at both ends of the SWCNT. These nanodiamonds on the hot and cold electrodes were labeled NDH and NDC, respectively. The thermometric setup is depicted in Fig. 1(c). A 532 nm laser was employed for excitation with a laser power set at $0.25 \,\mu W$, and an avalanche photodiode was utilized to measure the fluorescence intensity. Microwaves generated by Windfreak synthHD, featuring two machines with four sources, were amplified and irradiated across the entire substrate using a loop antenna attached to a $40\times$ objective lens. The substrate was positioned on a copper plate, which was heated from below by a large heater, allowing for the application of a gate voltage from the copper plate. During measurements, minor temperature fluctuations of 0.1 °C were observed, which were attributed to microwave exposure and environmental factors such as laboratory air conditioning. To maintain a consistent temperature on the copper plate without a cooling system, measurements were conducted at a temperature slightly above RT.

This study utilized four-point ODMR measurements [Fig. 1(d)],^{16,20)} a common technique for determining frequency shifts in ODMR (see supporting information). The temperature-dependent zero-field splitting frequency (D(T)) was ascertained by analyzing the fluorescent intensities at four microwave frequencies. A sequence pattern was established through data acquisition (DAQ) and controlled using a microwave switch. Measurements were executed by alternating among the four points, as illustrated in Fig. 1(e), and repeated for 160 s in total (40 s for each point) to eliminate the effects of fluorescence intensity fluctuations. After the four-point measurement, the position was adjusted to maximize fluorescence intensity for enhanced tracking of the nanodiamond; this adjustment process was repeated four times.

A current was supplied to local heaters to generate a temperature difference through joule heating. However, the four-point ODMR method initially struggled to accurately measure temperature due to magnetic fields generated by the heater current, drastically changing the shapes of the ODMR spectra (see supporting information). To address this, the current ratios of the three heaters were adjusted based on calculations using Ampere's law, as illustrated in Fig. 2(a). This adjustment aimed to cancel out the magnetic field at the positions of the two electrodes where the nanodiamonds were located. Figure 2(b) displays the calculated value of the © 2024 The Author(s). Published on behalf of



Fig. 2. (a) Schematic of the sample. The light blue, purple, and pink arrows on the local heaters show the direction of the current. The current direction of Heater 2 was opposite to that of Heaters 1 and 3 to nullify their magnetic fields. The current of each local heater was adjusted such that the ratio of the three heater currents was consistent. (b) Calculated magnetic field along the dotted line in (a), when the total current of 20 mA flowed through the three heaters. (c)–(d) ODMR spectra of NDH and NDC. A current of 20 mA flowed through the three heaters. The values obtained when a current flowed in the opposite direction are also indicated. The spectra were not split by the magnetic field when current was applied to the local heaters (shifted by joule heating).

magnetic field when each of the three heaters received a 20 mA current. The ODMR spectra for NDH and NDC, shown in Figs. 2(c) and 2(d), remained unchanged when current was applied to the heaters, confirming the effective-ness of the magnetic field cancellation and enabling accurate four-point ODMR measurements.

Subsequently, Seebeck measurements were performed. First, temperature differences were measured using the NV center. Since the temperature gradient of the ODMR center frequency for each nanodiamond varies by impurity concentration, strain, and surface geometry,¹⁵) it was essential to calibrate the system before using it as a thermometer. The substrate was heated using a large heater as shown in Fig. 1(c), and the frequency shifts were measured at both NDH and NDC [Fig. 3(a)]. The temperature dependence of zero-field splitting D(dD/dT) was observed to be proportional across the measured temperature range for both NDH and NDC, with values determined to be -71.3 ± 0.6 kHz K⁻¹ and



Fig. 3. (a) Temperature calibration results when a large heater changed the substrate temperature with the error bars representing the standard deviation. (b) Calculated temperatures of NDH and NDC as a function of local heater current. The value of the local heater represents the total value of the three local heaters, with the error bars representing the standard deviation. (c) Temperature difference obtained from (b) with the error bars representing the standard deviation. (d) Gate dependence of the sample. The source–drain voltage was 10 mV. (e) Measured voltage between two electrodes. The offset of the voltmeter was subtracted. (f) Voltage difference as a function of local heater current with the error bars representing the standard deviation.

 -64.1 ± 0.7 kHz K⁻¹, respectively. These values are consistent with previously reported gradients for nanodiamonds.¹⁵⁾

Next, the local temperature measurements were conducted while providing the local heater with a total current ranging from -20 to 20 mA with the substrate temperature fixed at 303 K. The electrode temperatures, adjusted using the calibration results [Fig. 3(a)], are depicted in Fig. 3(b). At the same current values, the temperature at the hot electrode consistently exceeded that at the cold electrode, indicating the local heater successfully established a temperature gradient across the SWCNT. The symmetry around 0 mA indicated that the direction of the current did not impact the four-point measurement, indicating that the magnetic field had been effectively neutralized. The Joule heat generated by the local heater was proportional to the square of the current, resulting in a quadratic curve. The temperature difference between NDH and NDC is shown in Fig. 3(c), where the temperature difference at 0 mA was not zero. The measurements depicted © 2024 The Author(s). Published on behalf of



Fig. 4. Voltage difference as a function of temperature difference, obtained from Figs. 3(c) and (f).

in Figs. 3(a) and 3(c) were conducted on different days, which might have contributed to variations in RT or other environmental factors.

Second, the voltage difference across the SWCNT was measured, with these measurements conducted in the absence of microwaves to minimize voltage noise. To characterize the electrical properties, we initially measured the transistor behavior of the SWCNT using the hot and cold electrodes as the source and drain, respectively, and applied the gate voltage from the back gate. The gate dependence of the SWCNT when a source–drain voltage of 10 mV was applied is shown in Fig. 3(d). The current remained relatively constant within the range of -1 to 1 V, indicating the metallic nature of the SWCNT, with a measured resistance of 430 k Ω . This value significantly exceeded two units of quantum conductance $4e^2/h$ ($R_Q = h/4e^2 = 6.5 \text{ k}\Omega$),¹⁹⁾ suggesting either potential damage to the SWCNTs or high contact resistance.

The voltage difference as the current of the local heater varied from -20 to 20 mA is shown in Fig. 3(e), with adjustments made for voltage offset. Measurements were repeated five times, yielding a standard deviation of approximately $2-5 \,\mu\text{V}$ for this SWCNT. Voltage was generated as current was applied to the heater. Furthermore, the SWCNTs displayed minimal gate dependence and were metallic. The voltage difference at a gate voltage of 0 V is depicted in Fig. 3(f), resulting in a quadratic curve similar to the analysis of the temperature difference.

Finally, the Seebeck coefficient was determined, as demonstrated in Fig. 4, using the temperature and voltage differences shown in Figs. 3(c) and 3(f). The measured thermoelectric force was almost directly proportional to the temperature difference. The Seebeck coefficient, calculated from the gradient of the dotted line, was $14.0 \pm 1.1 \,\mu V \, K^{-1}$, consistent with values obtained for both isolated²⁾ and bulk⁶⁾ metallic SWCNTs at RT. Notably, the Seebeck coefficient remains relatively stable between 303 and 310 K [the range

of the vertical axis in Fig. 3(b)] for metallic SWCNTs.⁶⁾ This confirms that the Seebeck coefficient can be accurately measured using nanodiamonds.

In this measurement, the standard deviation of the voltage difference was approximately $5 \,\mu$ V, and that of the temperature was approximately 0.4 K, which was comparable when converted to the Seebeck coefficient of $14 \,\mu$ V K⁻¹. This indicates that both temperature and voltage measurements comparably contributed to the overall accuracy. The accuracy of the temperature measurement can be enhanced by conducting measurements in a vacuum or by passivating the nanodiamonds. While measurements in ambient air offer greater versatility, conducting them in a vacuum eliminates fluctuations in ambient temperature and thermal conductance between the device and the nanodiamond. Additionally, the accuracy of temperature measurements can be improved through pulse measurements.²¹⁾

In this study, we conducted thermoelectric measurements on SWCNTs using nanodiamond quantum thermometry. The temperatures of the hot and cold electrodes were measured using nanodiamonds, and after canceling out the magnetic field, four-point measurements were feasible. The Seebeck coefficient was derived from the temperature and voltage differences between the two electrodes. For the metallic SWCNT, the measured Seebeck coefficient was $14.0 \pm 1.1 \,\mu V \, K^{-1}$. This innovative method is expected to reveal various thermoelectric effects of SWCNTs²²⁾ and can be applied to the thermoelectric measurements of various nanomaterials.

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