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# $3\omega$ method to measure thermal properties of electrically conducting small-volume liquid

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# 3$\omega$ method to measure thermal properties of electrically conducting small-volume liquid

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This work presents a method to measure the thermal conductivity and heat capacity of electrically conducting small-volume liquid samples using the 3$\omega$ technique. A mathematical model of heat transfer is derived to determine the thermal properties from the 3$\omega$ signal considering the device geometry. In order to validate the model, an experimental apparatus has been designed and set up to measure the thermal properties (thermal conductivity and heat capacity) of seven different liquid samples. The results show good agreement with other literature values, demonstrating that the suggested method is effective for measuring the thermal properties of electrically conducting liquids. More importantly, the result with a sample volume of 1 $\mu$l demonstrates the resolution of the thermal conductivity as precise as 0.01% which corresponds to a thermal-conductivity change of $10^{-4}$ W/m K in the case of water-based solutions. 
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## I. INTRODUCTION

Thermal properties of a liquid such as the thermal conductivity, thermal diffusivity and heat capacity are fundamental material properties. Particularly, the high demand for thermal analysis of a small-volume liquid sample is rapidly growing as liquid samples of small volume are getting more interest in microfluidics and bioengineering applications. Many researchers are trying to develop various schemes to measure the thermal properties of fluids with a small sample volume.[1–3] Traditionally, the transient hot-wire method is regarded as one of the standard techniques to determine the thermal conductivity and diffusivity of a fluid sample.[4] In the transient hot-wire method, a thin metallic wire, typically several centimeters in length, is immersed in the sample fluid and electrically heated while monitoring the resistance variation for the thermal response. Since the size of the wire is relatively large, the method requires a large volume of sample fluid (i.e., at least hundreds of milliliters) which is not desirable for expensive biosamples and functional materials. Also, many microfluidic applications demand more precise thermal analysis of microfluidic samples as they constantly pursue integration of multiple functionalities in a single device having small dimensions as in the micro-total-analysis-system ($\mu$-TAS) applications. In this regard, this work proposes a novel method to measure the thermal transport properties of an electrically conducting fluid with a sample volume as small as 1 $\mu$l.

Several methods using microfabrication techniques were developed in order to deal with the small sample volume in microfluidic applications.[1–3,5–8] Recently, we proposed a novel method based on laser heating of a microthermocouple tip, showing that the method is capable of determining the thermal conductivity of a 1 $\mu$l liquid sample.[8] However, the irregular shape of the thermocouple tip leads to an uncertainty up to ~10% in determining the thermal conductivity. The 3$\omega$ method offers a suitable way to characterize the thermal properties in microscale regime due to its high sensitivity and simplicity. The 3$\omega$ method uses a thin metallic strip patterned on the surface of a substrate which acts as both a heater and a sensor to detect the temperature response. The method has been widely used to measure the thermal conductivities of thin films and bulk solids.[9] Birge[5] employed the 3$\omega$ method with a thin planar heater immersed in a liquid to measure the frequency-dependent specific heat of the liquid, showing that the 3$\omega$ method can be applicable to thermal analysis of a liquid sample in the frequency domain. Moon *et al.*[6] also utilized the 3$\omega$ technique to measure the dynamic heat capacity and thermal conductivity of liquid, with several simplifying assumptions in the analysis of the temperature field. Recently, Chen *et al.*[7] designed a 3$\omega$ method to measure the thermal properties of solids and liquids under hydrostatic pressure by modeling the heat conduction from a finite thin strip located at the interface between the substrate and the liquid. However, all the above-mentioned methods are limited to dielectric liquids only and cannot be applied to electrically conducting liquids since a dielectric thin film needs to be deposited on the heater surface. Therefore, proper design of a 3$\omega$ device, along with a theoretical model which considers the dielectric layer to prevent an electrical leakage, is highly required to measure the thermal properties of the electrically conducting liquids.

In this work, we design a method for simultaneous measurement of the thermal conductivity and heat capacity of electrically conducting liquid samples based on the 3$\omega$ technique. The measuring device consists of a metallic strip and a dielectric thin film deposited on the surface of a glass substrate. The dielectric thin film insulates the metal film to prevent the electrical leakage. A heat conduction model is derived for the designed geometry along with a scheme to determine the thermal properties of the liquid samples.

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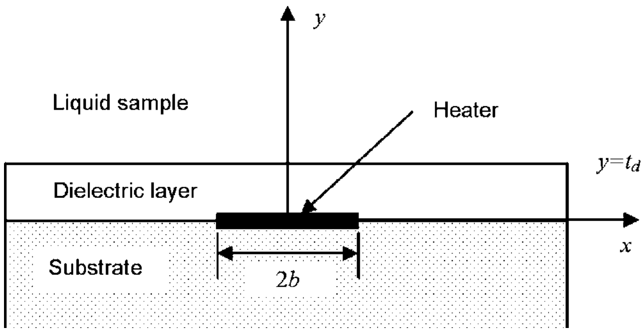


FIG. 1. Schematic diagram of the $3\omega$ technique for measuring the thermal properties of liquid.

## II. THEORY

### A. Heat conduction

Figure 1 displays the geometry of the $3\omega$ method. When an ac power of frequency $\omega$ is applied to a thin metallic strip of width $2b$, it generates Joule heating across the strip at the frequency $2\omega$. The heating then induces temperature oscillation at the same frequency of $2\omega$. Neglecting the convective heat loss to the surrounding fluid, the average temperature at the thin metallic strip can be expressed analytically as[9]

$$T = \frac{P}{l\pi}\int_0^\infty \frac{\sin^2(\lambda b)}{(\lambda b)^2}\tilde{T}(\lambda)d\lambda, \tag{1}$$

where $P$ and $l$ are the heating power and the length of the thin metallic strip, respectively. In Eq. (1), $\tilde{T}$ is the Fourier transformed temperature for an infinitely narrow line source with respect to the $x$ coordinate, which represents the thermal response of the medium whose thermal properties are to be measured.

An analytical solution for $\tilde{T}$ can be derived from the thermal properties of the individual layers and the boundary conditions at the interface. Several studies were devoted to solve the heat transfer problems for thermal analysis with various structures.[10–13] Assuming the uniform heat flux boundary condition at the strip and negligible thermal boundary resistance and thermal mass of the thin strip, we obtain the complex $\tilde{T}$ as follows. For the substrate,

$$\tilde{T}(\lambda) = \frac{1}{\kappa_s k_s}, \tag{2}$$

for the liquid/substrate,

$$\tilde{T}(\lambda) = \frac{1}{\kappa_l k_l + \kappa_s k_s}. \tag{3}$$

for the liquid/dielectric layer/substrate,

$$\tilde{T}(\lambda) = \frac{1}{\kappa_d k_d}\frac{(1+R_s)+(1-R_s)e^{-2k_d t_d}}{(1+R_l)(1+R_s)-(1-R_l)(1-R_s)e^{-2k_d t_d}}, \tag{4}$$

$$R_j = \frac{\kappa_j k_j}{\kappa_d k_d}, \tag{5}$$

where $k_j$ is the complex wave number defined as

$$k_j = \sqrt{\lambda^2 + i\frac{2\omega C_j}{\kappa_j}}. \tag{6}$$

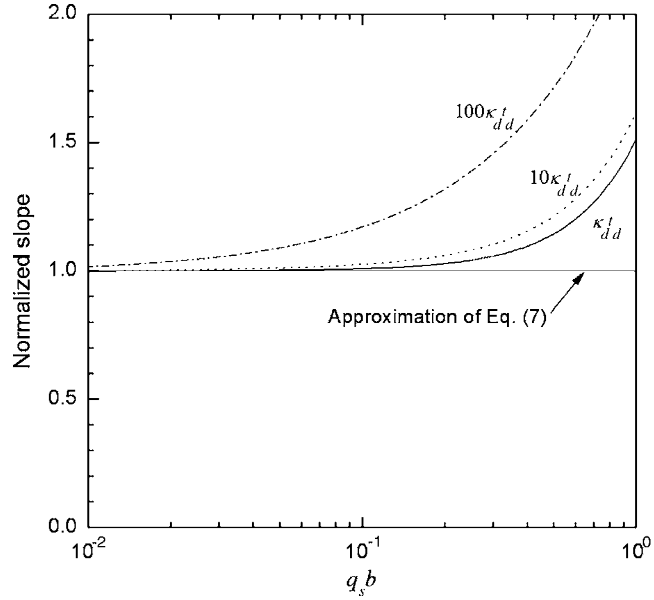


FIG. 2. Normalized slope of Eq. (7) as a function of $q_s b$. If the thermal penetration depth at the given frequency is larger than the width of the heater, the slope of the real part versus $\ln \omega$ is independent of the width of the strip, the heat capacity of the two neighbor mediums, and the thermal conductivity of the dielectric layer.

In the above equations, $\kappa_j$ and $C_j$ are the thermal conductivity and heat capacity of the $j$-labeled layer. The symbol $t_d$ refers to the thickness of the dielectric layer. Subscripts $s$, $l$, and $d$ correspond to the substrate, liquid, and dielectric layer, respectively.

### B. Scheme to determine the thermal property

To determine the thermal properties from a theoretical solution, a simple formula that directly exhibits thermal property dependence on the experimental data is preferred. For example, the transient hot-wire method uses the linear dependence of the increased temperature on the logarithm of time.[4] Similarly, Cahill[9] simplified Eqs. (1) and (2), showing that the real part of the temperature oscillation versus a logarithm of frequency offers a more reliable measure to determine the thermal conductivity of a substrate.

Similar approaches were taken for a liquid/substrate structure in the $3\omega$ measurement of the liquid thermal conductivity. In the computation of two-dimensional temperature field, Moon *et al.*[6] modeled the liquid/substrate structure as an effective medium whose apparent thermal conductivity is the sum of the thermal conductivities of the two media ($\kappa_{l+s} = \kappa_l + \kappa_s$). Recently, Chen *et al.*[7] also defined the apparent thermal conductivity to be the sum of the two components in their heat transfer model to determine the liquid thermal conductivity from the real part of the temperature response.

In this work, to find a simple relation, parametric studies are conducted with Eqs. (1) and (4) by varying the associated parameters. Figure 2 summarizes the results of the analysis. It shows the slope of the real part versus $\ln \omega$ of the tempera-

TABLE I. Evaluation of the errors dependent on the thermal conductivities for the individual media.

| $\kappa_l$ | $\kappa_d$ | $\kappa_s$ | Error (%) | Thermal-conductivity range (W/m K) |
|---|---|---|---|---|
| − | − | − | 0.11 | $\kappa_l$ |
| − | − | + | 0.04 | −: 0.1 |
| − | + | − | 2.92 | +: 1 |
| − | + | + | 1.28 | $\kappa_d$ |
| + | − | − | 0.00 | −: 0.5<br>+: 20 |
| + | − | + | 0.03 | $\kappa_s$ |
| + | + | − | 0.01 | −: 1 |
| + | + | + | 0.00 | +: 150 |

ture oscillation normalized by $-P/2\pi l(\kappa_l+\kappa_s)$ as a function of the nondimensional thermal penetration depth $q_s b$ (where $q_s^{-1}=\sqrt{\kappa_s/2\omega C_s}$). The results indicate that, if the thermal penetration depth at a given frequency is larger than the width of the heater and the heat conduction through the dielectric layer is negligible, the slope of the curve in the real part of the temperature versus ln $\omega$ plot depends on the thermal conductivities of the two neighboring media:

$$\kappa_l + \kappa_s = -\frac{P}{2l\pi}\frac{d \ln \omega}{dT_{\text{real}}}. \tag{7}$$

To confirm the validity of the above equation over wide range parameters, the error was calculated by varying the properties of the media. Since the thermal conductivity is more critical than the heat capacity, the thermal conductivities were varied to cover the entire range of practical materials. The results are summarized in Table I. It is evident that the approximation of Eq. (7) would offer a reliable measure on the thermal conductivity of a liquid. It is noted that even the worst possible combination (low conductivity of the liquid and high conductivity of the dielectric film) results in an error less than 3%.

Unlike the case of thermal-conductivity measurement, parameters such as the thermal conductivity of the dielectric layer play an important role in determining the heat capacity of a liquid. Accordingly, no simple relation can be used to determine heat capacity but a nonlinear least square method is utilized based on the theoretical model of Eq. (4). In the least square fitting, literature values[14] are used for the thermal properties of the substrate. The thermal conductivity of the liquid is calculated from Eq. (7). The thermal conductivity of the dielectric layer is measured using a reference liquid with well-known thermal properties. It can be shown that the heat capacity of the dielectric layer has negligible effect on the temperature oscillation because of the small mass.

## III. EXPERIMENT

The measuring device consists of a metallic strip and a dielectric thin film deposited on the surface of a Borofloat glass substrate (model Schott 33). A 300-nm-thick gold film is deposited using an e-beam evaporator along with a 30-nm-thick chromium film as an adhesion layer between the glass substrate and the gold film. The metal films are patterned by the standard photolithographic technique. The width and length of the metallic strip are 20 $\mu$m and 1 mm, respectively. After that, a 200-nm-thick silicon nitride film was deposited on the substrate by plasma enhanced chemical vapor deposition (PECVD) to provide electrical insulation between the metallic strip and the surrounding liquid. Measurements were conducted by immersing the measuring device in a bath of the liquid sample.

The experimental setup is similar to that for measuring the thermal conductivity of solid thin films.[15] An exception is that the electrical current from an internal source of a lock-in amplifier (Stanford Research Systems, model SR810) is directly supplied to the metallic strip without amplification. As the 3$\omega$ component of the signal is approximately 1000 times smaller than the $\omega$ component, the $\omega$ component is eliminated by adjusting the gain of a differential amplifier (Analog Devices, model AD620) with an input impedance of 10 G$\Omega$. The 3$\omega$ signal without the $\omega$ component is measured by the lock-in amplifier. The heating power is adjusted so that the maximum temperature at the metallic strip is lower than 2 K. The amplitude and phase of the temperature signal are detected repeatedly by varying the modulation frequency from 1.5 to 3000 Hz.

In particular, some liquid samples that can be prepared in the form of a microdroplet on the silicon nitride surface are also used to measure the thermal properties. This is possible because the thermal penetration depth in the liquid is far smaller than that in the solid or gas. In the case of water, the thermal penetration depth at a frequency of 1.5 Hz is 177 $\mu$m ($\sqrt{\kappa_l/2\omega C_l}$) and thus the sample volume of 1 $\mu$l is sufficient to perform an experiment. Note that a hemisphere with a volume of 1 $\mu$l corresponds to a radius of 789 $\mu$m, which is almost four times larger than the thermal penetration depth in de-ionized (DI) water. In the present work, the DI water, glycerol, and ethylene glycol are also employed in microdroplet measurements because they do not spread on the silicon nitride surface.

## IV. RESULTS AND DISCUSSION

The thermal conductivities of seven different liquids were measured to verify the present experimental setup and the analysis scheme of Eq. (7). Figure 3 exhibits the real and imaginary components of the temperature oscillation as a function of ln $\omega$ for DI water. The lines correspond to the theoretical fits using Eq. (4). For DI water, the effective thermal conductivity calculated from the slope using Eq. (7) is 1.691 W/m K. Subtracting the thermal conductivity of the glass substrate of 1.083 W/m K (Ref. 14) from the effective value, the thermal conductivity of DI water is determined to be 0.608 W/m K. The measured thermal conductivity of water is close to the literature value, 0.610 W/m K at 25 °C.[16] The same procedure was applied to the other liquids, as summarized in Table II and Fig. 4(a). The results also agree reasonably with the literature[16] and confirm the ability of the present method to measure the thermal conductivity of a liquid. The deviations from the reference values are within 1% for DI water, glycerol, and methanol and a maximum of 11% for 2-propanol. The relatively large deviation observed in the liquids with low thermal conductivity, such as 2-propanol,

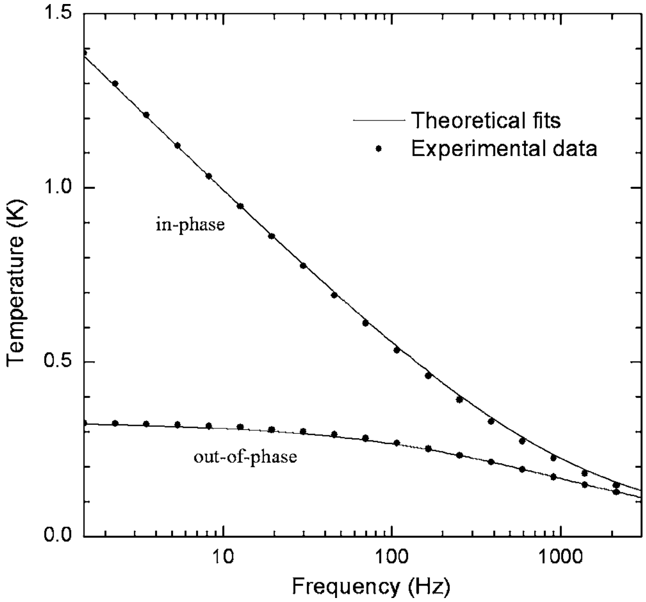


FIG. 3. Experimental data for DI water with the corresponding theoretical fits.

reflects the fact that the heat flow into a liquid sample is relatively small because of the low thermal conductivity of the liquid.

The heat capacities of the liquids were obtained simultaneously by the nonlinear least square fitting method. However, as mentioned earlier, the thermal conductivity of the dielectric layer needs to be determined prior to the heat capacity measurement since it is strongly dependent on the film thickness and the fabrication process.[15,17] In this work, DI water was used as a reference liquid to determine the thermal conductivity of the dielectric layer. The least square fitting scheme yields the thermal conductivity of the dielectric layer of 11.2 W/m K, which is far smaller than the bulk value but larger than the values for thin films deposited on a silicon substrate.[16,17] The results of heat capacity measurement are summarized in Table II and Fig. 4(b), with the corresponding reference values. The standard deviation for the heat capacity measurement was about 9%, which is substantially larger than that for the thermal conductivity. We believe that this relatively large uncertainty in the heat capacity measurement is mainly from the error in the input parameters for data analysis, such as the width of the strip and the thermal prop-

TABLE II. Experimental results.

| Test liquids (25 °C) | Experiments (W/m K) $\kappa_l$ | Experiments ($\times 10^6$ J/m$^3$ K) $C_l$ | Literature[a] (W/m K) $\kappa_l$ | Literature[a] ($\times 10^6$ J/m$^3$ K) $C_l$ |
|---|---|---|---|---|
| DI water | 0.608 | ⋯ | 0.610 | 4.17 |
| Glycerol | 0.293 | 2.93 | 0.292 | 3.12 |
| Ethylene glycol | 0.268 | 2.56 | 0.252 | 2.26 |
| Methanol | 0.200 | 2.04 | 0.202 | 2.02 |
| Ethanol | 0.171 | 1.93 | 0.182 | 2.06 |
| 1-propanol | 0.167 | 1.87 | 0.172 | 2.15 |
| 2-propanol | 0.139 | 2.19 | 0.156 | 2.36 |

[a]Reference 16.

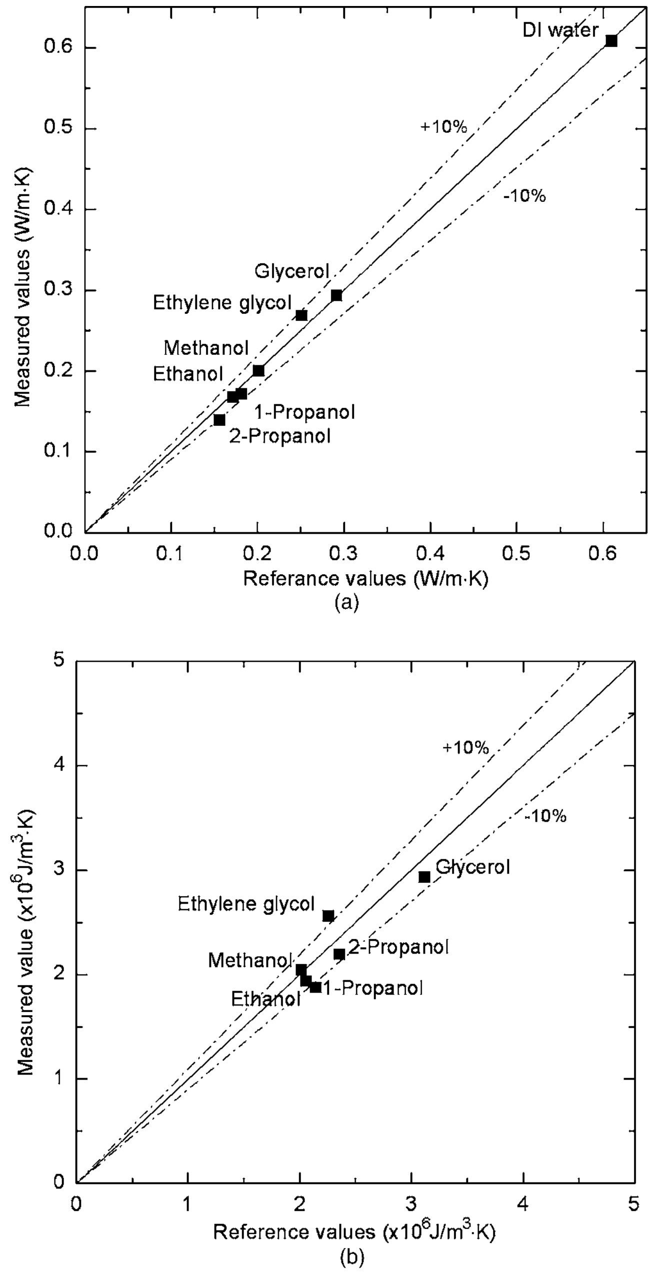


FIG. 4. Experimental results of (a) the thermal conductivity and (b) the heat capacity.

erties of the two neighboring media. Also, the lower sensitivity of the 3$\omega$ method to heat capacity than to thermal conductivity is partly responsible for the large uncertainty, which will be shown later in the sensitivity analysis.

Since DI water, glycerol, and ethylene glycol do not spread on the silicon nitride surface, their thermal properties were also measured with the sample prepared in the form of a microdroplet. The results reveal that there are no differences compared to those measured in the bulk liquid bath within an experimental resolution. For example, Fig. 5 displays the experimental results for DI water obtained by varying the sample volume. The sample volume larger than 1 $\mu$l shows no differences on the thermal conductivity. However, when the sample volume is below ~1 $\mu$l, it is difficult to measure the thermal conductivity of a liquid since the evaporation onto the surface significantly reduces the sample vol-

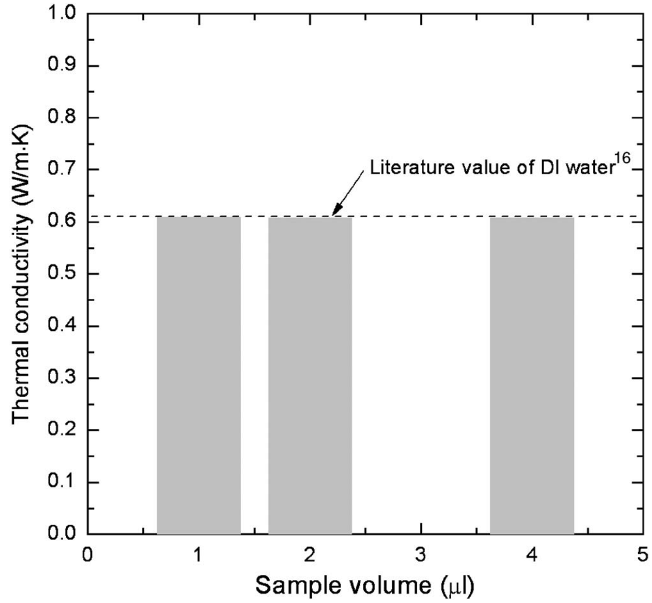


FIG. 5. Variations of the thermal conductivity with the sample volume for DI water.

ume due to the large area-to-volume ratio of a microdroplet. It is thus clear that the present method offers a reliable way to measure the thermal property of a liquid sample with a volume larger than 1 $\mu$l. Therefore, it would be particularly useful to small-volume samples such as nanofluids and biological samples, where the conventional transient hot-wire technique is not applicable as the sample volume is limited. Moreover, it is expected that proper chamber design to prevent evaporation of the liquid will provide measurements with a volume less than 1 $\mu$l.

To analyze the resolution of the measurement, experiments to measure the thermal conductivity of DI water were repeated ten times. The results are summarized in Fig. 6, exhibiting the deviations from the mean value. The maximum and the standard deviations of the measured data are 0.04% and 0.02%, respectively, which demonstrates that this

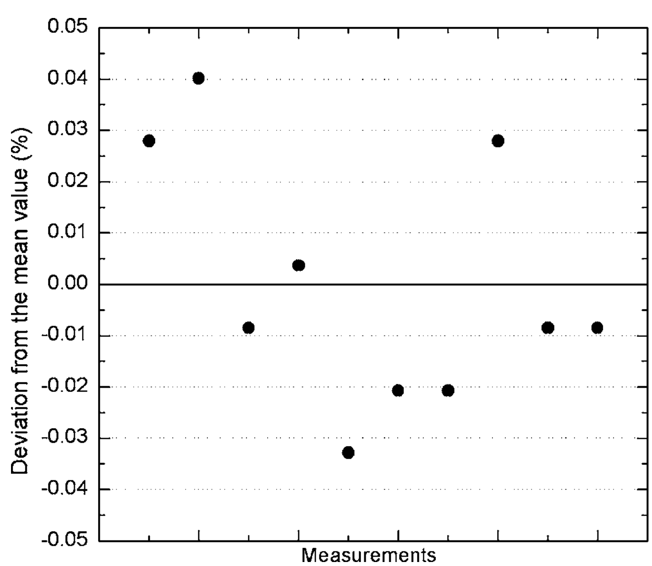


FIG. 6. Deviation of the experimental data for DI water.

TABLE III. Sensitivity parameters for four typical different substrates.

| Substrate [$\kappa_s$(W/m K), $C_s$(×10 J/m K)] | $\kappa_l$ | | $C_l$ | |
|---|---|---|---|---|
| | Real | Imag. | Real | Imag. |
| Air (0.026,0.0012) | 0.5942 | 0.7259 | 0.2715 | 0.1511 |
| Polyimide (0.12,1.55) | 0.5044 | 0.6273 | 0.2160 | 0.1191 |
| Glass (1.08,1.66) | 0.2865 | 0.3158 | 0.1444 | 0.0741 |
| Silicon (148,1.66) | 0.0177 | 0.0072 | 0.0164 | 0.0044 |

method is capable of measuring the thermal conductivity of typical liquids with a resolution on the order of 0.01%. The resolution of 0.01% corresponds to a sensitivity that can detect a thermal conductivity change of $10^{-4}$ W/m K in the case of water-based solutions. This resolution is far better than those of the traditional methods.

It is possible that a steady-state measurement gives rise to a natural-convection heat loss by the buoyant force. The natural-convection effect can be characterized by the Rayleigh number.[18] The Rayleigh number is defined based on the characteristic length $L$ of the geometry and the temperature difference $\Delta T$ in a fluid,

$$\mathrm{Ra}_L = \frac{g\beta\Delta T L^3}{\upsilon\alpha}, \tag{8}$$

where $g$ is the gravitational acceleration constant. $\beta$, $\upsilon$, and $\alpha$ are the thermal expansion coefficient, the kinematic viscosity, and the thermal diffusivity of a fluid, respectively. The critical Rayleigh number for the onset of natural convection is generally known to be $10^6$–$10^9$.[18] In this work, the Rayleigh number for the geometry in Fig. 1 is calculated to be $2.74\times10^{-4}$ for DI water with $\Delta T=2$ K and $L=20$ $\mu$m, which is much less than the critical Rayleigh number. Therefore, the natural-convection effect can be neglected in the present work, assuming the heat transfer within a liquid sample to be purely conductive.

As the sensitivity of the measurement is strongly affected by the substrate, the effect needs to be examined. The sensitivity parameter $S$ can be calculated from the temperature change $\Theta_n$ (real and imaginary parts) with respect to the thermal properties of liquid, i.e.,

$$S_{\kappa_l} = \left|\frac{\kappa_l}{E}\frac{\partial E}{\partial \kappa_l}\right|, \quad S_{C_l} = \left|\frac{C_l}{E}\frac{\partial E}{\partial C_l}\right|, \tag{9}$$

where $E$ is defined as the summation of $N$ different temperature responses:

$$E = \sum_{n=1}^{N} \Theta_n. \tag{10}$$

The sensitivity analysis was carried out for four common substrate materials—Borofloat glass, polyimide, silicon, and air (freestanding case). The results are listed in Table III, along with the thermal properties of the materials. Since the sensitivity is inversely proportional to the thermal conductivity of the substrate, air offers the best sensitivity. However, note that $SiN_x$ membranes larger than 1 mm in width are not generally self-standing. Consequently, Table III indicates that use of polymer substrates would lead to substantial increase in the sensitivity, compared to Borofloat glass which was chosen in this work for convenience in fabrication

In this work, a method to measure the thermal property of small-volume electrically conducting liquids has been proposed based on the $3\omega$ technique. Measurements demonstrate that the technique is capable of measuring the thermal properties of a microfluidic sample with a volume as small as 1 $\mu$l. Especially, the thermal conductivity can be measured with a resolution on the order of 0.01%. The suggested $3\omega$ technique can be applied to a variety of thermal-sensing applications where the conventional technique is not applicable as the sample volume is limited, e.g., nanofluids and biological samples.

## ACKNOWLEDGMENTS

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