Simultaneous measurement of thermal conductivity and heat capacity of bulk and thin film materials using frequency-dependent transient thermoreflectance method

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The increasing interest in the extraordinary thermal properties of nanostructures has led to the development of various measurement techniques. Transient thermoreflectance method has emerged as a reliable measurement technique for thermal conductivity of thin films. In this method, the determination of thermal conductivity usually relies much on the accuracy of heat capacity input. For new nanoscale materials with unknown or less-understood thermal properties, it is either questionable to assume bulk heat capacity for nanostructures or difficult to obtain the bulk form of those materials for a conventional heat capacity measurement. In this paper, we describe a technique for simultaneous measurement of thermal conductivity $\kappa$ and volumetric heat capacity $C$ of both bulk and thin film materials using frequency-dependent time-domain thermoreflectance (TDTR) signals. The heat transfer model is analyzed first to find how different combinations of $\kappa$ and $C$ determine the frequency-dependent TDTR signals. Simultaneous measurement of thermal conductivity and volumetric heat capacity is then demonstrated with bulk Si and thin film SiO$_2$ samples using frequency-dependent TDTR measurement. This method is further testified by measuring both thermal conductivity and volumetric heat capacity of novel hybrid organic-inorganic thin films fabricated using the atomic/molecular layer deposition. Simultaneous measurement of thermal conductivity and heat capacity can significantly shorten the development/discovery cycle of novel materials.

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I. INTRODUCTION

Thermal properties of nanostructures may deviate significantly from their bulk counterparts due to the size effects of electrons and phonons. There has been great interest in studying the thermal properties of thin films, which led to the development of various measurement techniques over the last two decades. The most widely used techniques are the 3-ω method, which utilizes periodic electrical heating on microfabricated metallic heaters and the transient thermoreflectance (TTR) methods including frequency-domain thermoreflectance (FDTR) method, and time-domain thermoreflectance (TDTR) method, which uses an ultrafast laser with a pulse width in the order of a few nanoseconds to tens of femtoseconds.

In the TTR methods, the heat capacity is often used as an input to obtain the thermal conductivity of the measured materials. As such, the accuracy of the thermal conductivity measurement depends strongly on the heat capacity input. Measuring the heat capacity of nanostructures such as thin films and nanowires is very challenging, which often requires time-consuming and costly micro/nano-fabrication steps. A common practice is adapting bulk values for the heat capacity of nanostructures, where the bulk values can be easily measured, such as using the differential scanning calorimeter. This is usually a reasonable assumption for most of the well-studied dense materials, such as aluminium (Al), silicon (Si), and silicon dioxide (SiO$_2$), since nanostructuring does not significantly change the heat capacity. However, for many new materials, it is either questionable to assume bulk heat capacity for thin films or difficult to obtain the bulk form of these new materials for a conventional heat capacity measurement.

The material development/discovery cycle could be significantly shortened if thermal conductivity and heat capacity of materials can be measured simultaneously or even just using the same equipment. Schmidt et al. showed that simultaneous measurement of thermal conductivity and heat capacity of bulk Si and sapphire samples using FDTR is possible if the difference between the sensitivities of these two properties is larger than 0.05.

In this paper, we demonstrate the realization of simultaneous measurement of thermal conductivity $\kappa$ and volumetric heat capacity $C$ for both bulk and thin film materials using a frequency-dependent TDTR method. This paper is organized as following. In Sec. II, the heat transfer model for frequency-dependent TDTR measurement is analyzed to find how different combinations of $\kappa$ and $C$ determine TDTR signals at different frequency ranges. Simultaneous measurement of thermal conductivity and volumetric heat capacity of bulk Si and SiO$_2$ thin film samples are demonstrated in Secs. III A and III B, respectively. In Sec. III C, this method is extended to measure thermal conductivity and volumetric heat capacity of a novel hybrid organic-inorganic multilayer thin film.

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material fabricated using the atomic/molecular layer deposition (ALD/MLD).

II. HEAT TRANSFER ANALYSIS

To analyze the possibility for simultaneous measurement of thermal conductivity and heat capacity of bulk and thin film materials, we start with the heat transfer model in typical sample configurations of TTR measurements. Figure 1(a) shows the working principle of a typical ultrafast laser-based TDTR measurement. In our work, we used Spectra-Physics Tsunami femtosecond Ti-sapphire laser which emits a train of 150 fs pulses at a repetition rate of 80 MHz. The laser output is divided into pump and probe beams. The pump beam thermally excites a sample and the probe beam measures the changes of the reflectivity, which is temperature-dependent.

The pump beam passes through an electro-optic modulator (EOM) that modulates the beam at a frequency between 0.1 and 20 MHz so that the signals can be detected by a photodetector and a lock-in amplifier. By changing the optical path length through a mechanical moving stage, the probe beam arrives at the sample surface at a different time interval after the pump beam. The temporal decay of the optical signals is measured and used to deduce the thermal properties with a heat transfer model through a multi-parameter fitting process. The details of experiment setup and the data reduction scheme have been presented in literature.

Figures 1(b) and 1(c) show the schematics of the typical bi-layer (for bulk materials) and tri-layer (for thin films) sample configurations used in TTR techniques, respectively. The bi-layer structure consists of a metallic thin film and a substrate with unknown thermal properties. Similarly, the tri-layer structure consists of a metallic thin film, a thin film with unknown thermal properties, and a substrate with known thermal properties. The metallic thin films with a thickness of ~100 nm are usually deposited on the samples, which serves both as an energy absorber for the laser beams and as the temperature transducer for the probe beam. The heat of the pump beam is absorbed by the surface of the metallic layer, and then conducted through the layers and interfaces in the sample. In Sec. II A, the heat transfer model based on the transform matrix method for heat transfer through layers and interfaces and the lock-in signal are presented. More details are placed in the Appendix to ease the reading.

A. Heat transfer model and lock-in signal

Considering a cylindrical heating spot on the metallic transducer that absorbs pulsed laser heating, e.g., Figs. 1(b) and 1(c), the transient heat conduction equation for each layer can be written as the following:

$$\frac{\kappa_r}{r} \frac{\partial}{\partial r} \left[ r \frac{\partial \bar{\theta}(r, z)}{\partial r} \right] + \kappa_z \frac{\partial^2 \bar{\theta}(r, z)}{\partial z^2} = C \frac{\partial \bar{\theta}(r, z)}{\partial t}, \quad (1a)$$

where $r$ is the radial coordinate, $z$ is the cross-plane coordinate (in the depth direction), $t$ is time, $\bar{\theta}$ is the temperature, $C$ is the volumetric heat capacity, and $\kappa_r$ and $\kappa_z$ are the in-plane and cross-plane thermal conductivity, respectively. To solve the equation with radial symmetry, the zeroth-order Hankel transform is performed to simplify Eq. (1a), which yields

$$-\kappa_r x^2 \bar{\theta}(z) + \kappa_z \frac{\partial^2 \bar{\theta}(z)}{\partial z^2} = C \frac{\partial \bar{\theta}(z)}{\partial t}, \quad (1b)$$

where $x$ is the Hankel transform variable, and $\bar{\theta}$ is the temperature in the Hankel transform. Due to the periodic laser heating at the modulation frequency $\omega$, the solution for the temperature field in Eq. (1b) should depend on the modulation frequency. Applying the Fourier transform, Eq. (1b) becomes

$$\frac{\partial^2 \bar{\theta}(\omega, z)}{\partial z^2} = q_j^2 \bar{\theta}(\omega, z), \quad (2)$$

where $\bar{\theta}(\omega, z)$ is the temperature at any arbitrary point $z$ in the depth direction at the modulation frequency $\omega$, and the thermal wave vector $q_j$ of the $j$th layer is

$$q_j = \sqrt{\frac{\kappa_r x^2 + iC\omega}{\kappa_z}} = \sqrt{\frac{\kappa_{rj} x^2 + i\omega}{\kappa_{zj} D_{zj}}}, \quad (3)$$

where $\kappa_{rj}$ and $\kappa_{zj}$ are the in-plane and cross-plane thermal conductivity of the $j$th layer, respectively. $C_j$ is the volumetric heat capacity of the $j$th layer. $D_{zj}$ is the cross-plane thermal conductivity.
diffusivity of the jth layer, i.e., \( D_{j} = \kappa_{j} / C_{j} \). The transform method described by Carslaw and Jaegar\(^{17} \) is adopted to solve the heat conduction equation in a multilayer structure. The temperature of the sample surface is given as

\[
\theta_{1} = -\frac{D^{+}}{C^{+}} F_{1},
\]

where \( \theta_{1} \) and \( F_{1} \) are the temperature and heat flux on the top side of the multilayer stack, \( C^{+} \) and \( D^{+} \) are the elements of the transform matrix, which is calculated in detail in the Appendix.

The frequency-domain thermal response \( H(\omega) \) of the surface temperature change in real space can then be found by taking the inverse Hankel transform of Eq. (4) with the weighting using the probe intensity distribution which is taken as a Gaussian spot (see the Appendix for details):

\[
H(\omega) = \frac{v \rho_{p} Q_{\text{pump}}}{2\pi} \int_{0}^{\infty} x \left( -\frac{D^{+}}{C^{+}} \right) \exp \left( -\frac{x^{2} R_{pp}}{8} \right) dx,
\]

where \( v \) is the thermoreflectance coefficient of the metal transducer; \( Q_{\text{pump}} \) and \( Q_{\text{probe}} \) are the power absorbed from pump and probe beams, respectively,

\[
R_{pp} = R_{\text{pump}}^{2} + R_{\text{probe}}^{2},
\]

where \( R_{\text{pump}} \) and \( R_{\text{probe}} \) are the 1/e\(^2\) radius of pump and probe beam intensity distribution as a Gaussian spot, respectively. Similar to the analysis in Ref. 9, the upper limit \( x_{\text{max}} \) of the integral in Eq. (5) can be set to

\[
x_{\text{max}} = \sqrt{\frac{32}{R_{pp}}} \quad \text{(6b)}
\]

without a significant loss of accuracy since \((-\frac{D^{+}}{C^{+}}) \exp(-\frac{x^{2} R_{pp}}{8})\) decreases rapidly when \( x \) gets larger.

A lock-in amplifier picks up the fundamental harmonic component of the probe signal \( Z(\omega) \) at the modulation frequency \( \omega \) and rejects all other components. In the case of pulsed pump and probe beams, \( Z(\omega) \) is given as

\[
Z(\omega) = \sum_{N=-\infty}^{\infty} H(\omega + N \omega_{s}) \exp(iN \omega_{s} \tau),
\]

where \( N \) is an integer, \( \omega_{s} \) is the probe pulsing frequency, \( \tau \) is the delay time between the arrival of the probe and pump pulses to the sample surface, and \( H(\omega + N \omega_{s}) \exp(iN \omega_{s} \tau) \) is the weighted sampling frequency-domain response of the surface temperature change in real space. The largest contribution for the sum in Eq. (7) is the response at the modulation frequency \( H(\omega) \). Similar to Ref. 9, the ratio of the in-phase signal \( V_{i} \), and out-of-phase signal \( V_{o} \),

\[
\frac{V_{i}}{V_{o}} = -\text{Re}(Z(\omega))/\text{Im}(Z(\omega)),
\]

is used in this work as the measurement signal for data analysis since the experimental errors due to the fluctuation in laser power are minimized and measuring the values of \( v, Q_{\text{pump}}, \) and \( Q_{\text{probe}} \) can be avoided.

In Secs. II B and II C, we analyze how different combinations of \( \kappa \) and \( C \) determine the thermal response \( H(\omega) \) in TDTR signals at different modulation frequency ranges for the bi-layer and tri-layer sample configurations, respectively.

**B. Bulk samples**

For a bi-layer structure (bulk samples), the term \(-D^{+}/C^{+}\) in the thermal response \( H(\omega) \) is calculated by substituting the matrix elements for each layer or interface for the transform matrix, which is

\[
-\frac{D^{+}}{C^{+}} = \frac{\gamma_{3} m + \gamma_{3} + 1}{\gamma_{3} \left( \frac{2}{\gamma_{1}} \right) + \gamma_{3} m + m},
\]

where \( m = \tan(\eta_{1} \delta_{1}) \) with the thermal wave vector \( \eta_{1} \) as defined in Eq. (3) and the thickness \( \delta_{1} \) of the metallic transducer film, \( G_{2} \) is the interfacial thermal conductance between the metallic film and the bulk substrate, \( \gamma_{1} = \kappa_{1} / \kappa_{3} \) with the cross-plane thermal conductivity of the metallic film \( \kappa_{1} \) and \( \gamma_{3} = \kappa_{3} / \kappa_{3} \) with the thermal wave vector \( \kappa_{3} \) as defined in Eq. (3) and the cross-plane thermal conductivity \( \kappa_{3} \) of the substrate.

From Eqs. (5) and (9), the dominant thermal property in the thermal response \( H(\omega) \) can be analyzed by considering the \( \gamma_{3} \) term, which is the only variable related to the unknown thermal properties of the target bulk substrate to be measured. Generally, this analysis compares the averaged beam spot radius \( \sqrt{R_{pp}} \) with the radial thermal diffusion length \( L_{r} \), to identify whether the heat transfer is more dominant in the radial direction or in the cross-plane direction. The radial thermal diffusion length \( L_{r} \) is defined as

\[
L_{r} = \sqrt{2\kappa_{3}/\omega C_{3}},
\]

where \( \kappa_{3} \) and \( C_{3} \) are the thermal conductivity in the radial direction and the volumetric heat capacity of the bulk substrate, respectively.

When the radial thermal diffusion length is much smaller than one fourth of the averaged beam spot radius,

\[
L_{r} \ll \frac{1}{4} \sqrt{R_{pp}},
\]

radial heat transfer can be neglected. Considering that \( \sqrt{R_{pp}} \) is related to \( x_{\text{max}} \) by Eq. (6b), Eq. (11a) can be rewritten as

\[
L_{r}^{2} \ll \frac{2}{x_{\text{max}}^{2}} \sim \frac{2}{x^{2}}.
\]

The \( \gamma_{3} \) term in Eq. (9) then becomes

\[
\gamma_{3} = \kappa_{3} q_{3} = \kappa_{3} \sqrt{\kappa_{3} x^{2} / \kappa_{3} + i \omega C_{3} / \kappa_{3}}
\]

\[
= \sqrt{\kappa_{3} x^{2} + i \omega C_{3} x^{2}}
\]

\[
= i \omega C_{3} \left( 1 - x^{2} L_{r}^{2} / 2 \right) \approx i \omega C_{3}.
\]

This simplification tells that the thermal response is determined by the thermal effusivity \( \sqrt{\kappa_{3} C_{3}} \) at the high frequency limit when

\[
\omega \gg \frac{32 q_{3}}{R_{pp} C_{3}}.
\]

Here, Eq. (11d) is obtained by plugging Eq. (10) into Eq. (11a). Under this condition, the thermal effusivity \( \sqrt{\kappa_{3} C_{3}} \) determines the one-dimensional plane wave solution under the periodic planar heating condition, because the radial heat transfer can be neglected.\(^{8,9,17} \)
TABLE I. Dominant thermal properties in the thermal response at different ranges of modulation frequency $\omega$ in a bi-layer sample configuration (bulk materials).

<table>
<thead>
<tr>
<th>Thermal wave solution</th>
<th>Quasi-steady three-dimensional spherical wave</th>
<th>One-dimensional plane wave</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega$</td>
<td>$\omega \ll \frac{3\kappa r_3}{R_{pp} C_3}$</td>
<td>$\omega \sim \frac{3\kappa r_3}{R_{pp} C_3}$</td>
</tr>
<tr>
<td>$L_r \leq \sqrt{R_{pp}}$</td>
<td>$L_r \geq \frac{1}{2} \sqrt{R_{pp}}$</td>
<td>$L_r \sim \frac{1}{2} \sqrt{R_{pp}}$</td>
</tr>
<tr>
<td>$\gamma_3$</td>
<td>$\sqrt{\kappa r_3 k_{3,3} x}$</td>
<td>$\sqrt{\kappa r_3 k_{3,3} x^2 + i\omega \kappa_3 C_3}$</td>
</tr>
<tr>
<td>Thermal property</td>
<td>$\sqrt{\kappa_3 \kappa_5}$</td>
<td>$\sqrt{\kappa_3 \kappa_5}$</td>
</tr>
</tbody>
</table>

When the radial thermal diffusion length is much larger than one fourth of the averaged beam spot radius,

$$L_r \gg \frac{1}{4} \sqrt{R_{pp}},$$

(12a)

radial heat transfer dominates the transport. Equation (12a) can be rewritten as

$$L_r^2 \gg \frac{2}{\gamma_3} \approx \frac{2}{\gamma_3},$$

(12b)

The $\gamma_3$ term in Eq. (9) then becomes

$$\gamma_3 = \sqrt{\kappa r_3 k_{3,3} x^2 + i\omega \kappa_3 C_3} \approx \sqrt{\kappa r_3 k_{3,3} x}.$$  

(12c)

This simplification tells that the thermal response is determined by the averaged thermal conductivity $\sqrt{\kappa r_3 k_{3,3}}$ at the low frequency limit when

$$\omega \ll \frac{3\kappa r_3}{R_{pp} C_3}.$$  

(12d)

Here, Eq. (12d) is obtained by plugging Eq. (10) into Eq. (12a). Under this condition, the averaged thermal conductivity $\sqrt{\kappa r_3 k_{3,3}}$ determines the three-dimensional spherical-wave quasi-steady state solution under a periodic point source heating condition, because radial heat transfer is dominant.\textsuperscript{8}

When the radial thermal diffusion length is comparable to one fourth of the averaged beam spot radius, i.e., $L_r \sim \frac{1}{4} \sqrt{R_{pp}}$, both thermal conductivity $\sqrt{\kappa r_3 k_{3,3}}$ and thermal effusivity $\sqrt{\kappa_3 C_3}$ play a role in the measured thermal response.

Table I summarizes the above analysis, i.e., how different combinations of thermal conductivity and heat capacity determine the thermal response at different ranges of modulation frequency $\omega$ in a bi-layer sample configuration. It is challenging to simultaneously measure the thermal conductivities $\kappa_3$ and $\kappa_5$ in both radial (in-plane) and cross-plane directions and the heat capacity $C_3$ since the thermal responses are only determined by the two combinations of these three unknowns, which are thermal conductivity $\sqrt{\kappa r_3 k_{3,3}}$ and thermal effusivity $\sqrt{\kappa_3 C_3}$. However, if the target material with unknown thermal properties is nearly isotropic $(\kappa_3 \approx \kappa_5)$ or with a known anisotropy $(\kappa_3 k_{3,3})$, it could be straightforward to extract the two unknown thermal properties $\kappa_3$ and $C_3$ using the thermal response.

### C. Thin film samples

For a tri-layer structure (thin film samples), the term $-D^+ / C^+$ in the thermal response $H(\omega)$ is calculated by substituting the matrix elements for each layer or interface for the transform matrix, which is,

$$-D^+ / C^+ = \frac{m \left( \frac{\beta}{\gamma_1} + \frac{\beta}{\gamma_2} + \frac{n}{\gamma_1} + \frac{n}{\gamma_2} \right) + \frac{\beta}{\gamma_2} + \frac{\beta}{\gamma_3} + \frac{\beta}{\gamma_1} + \frac{n}{\gamma_1} + \frac{n}{\gamma_2} + \frac{n}{\gamma_3} + 1}{\gamma_1 \left( \frac{\beta}{\gamma_1} + \frac{\beta}{\gamma_2} + \frac{n}{\gamma_1} + \frac{n}{\gamma_2} + m \left( \frac{\beta}{\gamma_1} + \frac{\beta}{\gamma_2} + \frac{n}{\gamma_1} + \frac{n}{\gamma_2} + \frac{n}{\gamma_3} + 1 \right) \right)},$$

(13)

where $m = \tanh (q_1 d_1)$ with $d_1$ defined as the thickness of the metallic film, $n = \tanh (q_3 d_3)$ with $d_3$ defined as the thickness of the thin film, $\gamma_1 = q_1 \kappa_1$ with $\kappa_1$ as the cross-plane thermal conductivity of the metallic film, $\gamma_3 = q_3 \kappa_3$ with $\kappa_3$ as the cross-plane thermal conductivity of the metallic film, $\gamma_5 = q_5 \kappa_5$ with $\kappa_5$ is the cross-plane thermal conductivity of the substrate, $G_2$ is the interfacial thermal conductance between the metallic film and the thin film, $G_4$ is the interfacial thermal conductance between the thin film and the substrate.

Here $q_j$ ($j = 1, 3, 5$) is the thermal wave vector defined in Eq. (3). Apparently the thermal properties of the target layer are reflected in the thermal response $H(\omega)$ through $\gamma_j n$ and $n/\gamma_j$ terms in Eq. (13).

When the in-plane thermal diffusion length in the target thin film layer is much smaller than one fourth of the averaged beam spot radius,

$$L_r \ll \frac{1}{4} \sqrt{R_{pp}},$$

(14a)

the cross-plane heat transfer dominates the heat transfer through the thin film layer. Similar to Eqs. (11b) and (11c), the \( \gamma_3 \) term in Eq. (13) can then be simplified to

\[
\gamma_3 = \frac{\kappa_3 q_3}{\kappa_3} = \frac{\kappa_3 \sqrt{\kappa_3 x^2 / \kappa_3} + i \omega C_3 / k_3}{\sqrt{\kappa_3 x^2 / \kappa_3}}
\]

\[
\approx \frac{i \omega C_3}{\kappa_3} \sqrt{1 - i x^2 L_z^2 / 2} \approx i \omega C_3 / \kappa_3.
\]

Accordingly under the condition of Eq. (14a),

\[
q_3 = \gamma_3 / \kappa_3 \approx \frac{i \omega C_3}{\kappa_3} = i \omega / D_3.
\]

Such simplifications can always be satisfied by choosing the pump and probe spot radius to ensure that \( \sqrt{R_{pp}} \approx 4 L_z \). Assuming a typical heat capacity of 2 J/cm\(^2\) K and the thermal conductivity of the thin film layer smaller than 10 W/m K, which is true for most of nanostructured materials other than carbon nanotubes and graphene, Eqs. (14a) and (14c) are valid for a wide range of modulation frequency 0.1–20 MHz if the radii of pump beam and probe beam are larger than 15 \( \mu \)m and 5 \( \mu \)m. This also confirms that most of thermal conductivity measurements in thin films are cross-plane for a wide range of modulation frequency.\(^5,13\)

The terms \( \gamma_3 \) and \( n / \gamma_3 \) in Eq. (13) can then be analyzed by comparing the thickness \( d_3 \) of the target thin film layer to the thermal penetration depth \( L_z \), to determine whether the thermal wave penetrates into a limited depth of the layer or throughout the layer. The thermal penetration depth \( L_z \) in the \( j \)th layer, induced by the frequency modulation of the pump beam, is written as\(^13\)

\[
L_z = \sqrt{2 D_{3j} / \omega},
\]

where \( D_{3j} \) is the cross-plane thermal diffusivity of the \( j \)th layer. The term \( n / \gamma_3 \) can be simplified according to the two limit cases of the tanh function (when \(|a| \leq 1/3, \tan(a) \approx a\); when \(|a| \geq 3, \tan(a) \approx 1\)) as

\[
\frac{n}{\gamma_3} = \frac{\tanh(q_3 d_3)}{\sqrt{\kappa_3 C_3}} = \frac{1}{\sqrt{\kappa_3 C_3}} \tanh\left( \frac{i \omega C_3}{\kappa_3 d_3} \right) = \frac{1}{\sqrt{\kappa_3 C_3}} \tanh\left( \sqrt{2 i} \frac{d_3}{L_z} \right)
\]

\[
\approx \frac{1}{\sqrt{\kappa_3 C_3}}, \quad \text{when } \left| \frac{i \omega C_3}{\kappa_3 d_3} \right| \geq 3 \quad \text{or } \left| \sqrt{2 i} \frac{d_3}{L_z} \right| \geq 3.
\]

Similarly, the term \( n / \gamma_3 \) can be simplified as

\[
\frac{n}{\gamma_3} = \tanh(q_3 d_3) \sqrt{\kappa_3 C_3} = \tanh\left( \frac{i \omega C_3}{\kappa_3 d_3} \right) \sqrt{\kappa_3 C_3} = \frac{1}{\sqrt{\kappa_3 C_3}} \tanh\left( \sqrt{2 i} \frac{d_3}{L_z} \right)
\]

\[
\approx \frac{1}{\sqrt{\kappa_3 C_3}}, \quad \text{when } \left| \frac{i \omega C_3}{\kappa_3 d_3} \right| \geq 3 \quad \text{or } \left| \sqrt{2 i} \frac{d_3}{L_z} \right| \geq 3.
\]

With the condition \(|\sqrt{2 i} d_3 / L_z| \geq 3 \) in Eqs. (16a) and (16b), we found that when

\[
L_z / d_3 \leq 0.47,
\]

the thin film layer can be viewed as semi-infinite, i.e., the thermal wave penetrates into a limited depth \( L_z \) of the target thin film layer. The terms \( n / \gamma_3 \) and \( \gamma_3 \) in Eq. (13) can then be simplified to \( 1 / \sqrt{\kappa_3 C_3} \) and \( \sqrt{\kappa_3 C_3} \), respectively. This simplification tells that the thermal response is essentially determined by the thermal effusivity \( \kappa_3 C_3 \) at the high frequency limit when

\[
\omega > 9 \frac{\kappa_3}{d_3^2 C_3}.
\]

Here, Eq. (17b) is obtained by plugging Eq. (15) into Eq. (17a). In such case, the data reduction for thin film measurement is similar to the bulk analysis (Sec. II B) since the thermal wave does not penetrate beyond the thin film layer.

With the condition \(|\sqrt{2 i} d_3 / L_z| \leq 1 \) in Eqs. (16a) and (16b), we found that when

\[
L_z / d_3 \geq 4.24,
\]

the thin film layer can be regarded as an interface layer since the heat diffuses deeply into the substrate. The terms \( n / \gamma_3 \) and \( \gamma_3 \) in Eq. (13) can then be simplified to \( d_3 / \kappa_3 \) and \( i \omega d_3 C_3 \), respectively. This simplification tells that the thermal response is determined by the thermal resistance \( d_3 / \kappa_3 \) and the heat capacity \( C_3 \) when the modulation frequencies \( \omega \) satisfies this condition:

\[
\frac{32 \kappa_3}{R_{pp} C_3} \ll \omega < \frac{0.11 \kappa_3}{d_3^2 C_3}.
\]
Here, Eq. (18b) is obtained by plugging Eq. (15) into Eq. (18a) and combining with Eq. (12d).

When the modulation frequency is in between the ranges defined in Eqs. (17b) and (18b), the terms \( n/\gamma_3 \) and \( \gamma_3 n \) in Eq. (13) cannot be simplified and both thermal diffusivity \( \kappa_{23}/C_3 \) and thermal effusivity \( \sqrt{\kappa_{23}C_3} \) play a role in the thermal response.

Table II summarizes the above analysis, i.e., how different combinations of thermal conductivity and heat capacity determine the thermal response at different ranges of modulation frequency \( \omega \) in a tri-layer sample configuration.

### D. \( \kappa \)-\( C \) diagram for simultaneous measurement of \( \kappa \) and \( C \)

A conventional TDTR measurement is usually performed with a single modulation frequency for the measurement of thermal conductivity \( \kappa \) of materials and the interfacial thermal conductance \( G \) using heat capacity \( C \) as input. Cahill et al. showed that \( \kappa \) and \( G \) can be independently extracted at different delay times for both bulk and thin films.18 Our previous FDTTR measurements7 on thin films showed that \( \kappa \) and \( G \) can be extracted at different modulation frequency ranges due to the different sensitivities of these two properties. Considering that the accurate extraction of the interfacial thermal conductance might affect the determination of \( \kappa \) and \( C \), in this work, we extract \( \kappa \) and \( C \) either at a range of modulation frequencies where the measured signal is insensitive to the interfacial thermal conductance or at a range of delay times where the interfacial thermal conductance can be extracted first.

Based on the analysis in Secs. II B and II C, we propose to conduct the TDTR measurement at different modulation frequencies for simultaneous measurement of \( \kappa \) and \( C \) for both bulk and thin film materials. At each modulation frequency, multiple pairs of \( \kappa \) and \( C \), which satisfies the different combinations of the analysis in Secs. II B and II C, can fit the TDTR signals. Such pairs of \( \kappa \)-\( C \) for each modulation frequency are then presented together as a curve in the “\( \kappa \)-\( C \)” diagram where many curves are presented for the measurement at different modulation frequencies. Then the cross-point on the \( \kappa \)-\( C \) diagram for different modulation frequencies gives a unique set of \( \kappa \) and \( C \), which represents the measured value of thermal conductivity and heat capacity of the material.

### III. RESULTS AND DISCUSSIONS

In this section, the simultaneous measurement of thermal conductivity and heat capacity is demonstrated for both bulk Si and thin film SiO\(_2\) samples. The method is then extended to measure the thermal properties of hybrid organic-inorganic thin film samples fabricated using ALD/MLD.

#### A. Bulk Si

A 350 \( \mu \)m thickness \( n \)-type (100)-orientated Si wafer was first cleaned with 5% HF solution to remove the native oxide and then coated with a 100 nm Al film by thermal evaporation. The thermal properties of Si at 300 K were measured using frequency-dependent TDTR method. The radii of pump and probe beam were chosen to be 15 \( \mu \)m and 5 \( \mu \)m, respectively.

We determined first the interfacial thermal conductance \( G_2 \), Figure 2(a) shows the calculated sensitivity of \(-V_{in}/V_{out}\) signal to the thermal properties of bulk Si at 6.8 MHz. Similar to Ref. 18, the sensitivity \( S_p \) of \(-V_{in}/V_{out}\) signal to the thermal property \( p \) is defined as

\[
S_p = \frac{d(-V_{in}/V_{out})}{d(-V_{in}/V_{out})},
\]

where \( d(-V_{in}/V_{out})/(-V_{in}/V_{out}) \) is the fluctuation of \(-V_{in}/V_{out}\) signal and \( p \) is the property that we are interested in measuring, which could thus be thermal conductivity, heat capacity, or interface thermal conductance in the multilayer structure presented in Fig. 1. Clearly, the \(-V_{in}/V_{out}\) signal is very sensitive to the interfacial thermal conductance \( G_2 \), but relatively insensitive to thermal conductivity \( \kappa_{23} \) and heat capacity \( C_3 \), at the delay time range of 4–7 ns. Using the measurement data for delay time at 4–7 ns, the interfacial thermal conductance is fitted to be 215 MW/m\(^2\) K, which is in line with the literature values of 116–350 MW/m\(^2\) K depending on sample surface and deposition conditions.6,19,20

Figure 2(b) shows the TDTR experiment data and the best-fit results of \(-V_{in}/V_{out}\) with modulation frequencies at 0.5 MHz, 0.98 MHz, and 6.8 MHz. Figure 2(c) shows the \( \kappa \)-\( C \) diagram with fitted \( \kappa_{23} \) and \( C_3 \) under each frequency, where multiple pairs of \( \kappa_{23} \) and \( C_3 \) satisfy the best-fit with the experiment data when only one single frequency measurement is conducted. For instance, the \( \kappa \)-\( C \) pairs of (1.4, 159), (1.59, 140), (1.8, 123.67) fit the experiment data collected at

| TABLE II. Dominant thermal properties in the thermal response at different ranges of modulation frequency \( \omega \) in a tri-layer sample configuration (thin film materials). |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Penetration depth of thermal waves | Penetrating throughout the layer | \( 0.11 \frac{\kappa_{23}}{dC_3} < \omega < 9 \frac{\kappa_{23}}{dC_3} \) | Penetrating into a limited depth of the layer | \( \omega \geq 9 \frac{\kappa_{23}}{dC_3} \) |
| \( \omega \) | \( \frac{3\kappa_{23} z}{\kappa_{13} C_3} \ll \omega < 0.11 \frac{\kappa_{23}}{dC_3} \) | \( 0.11 \frac{\kappa_{23}}{dC_3} < \omega < 9 \frac{\kappa_{23}}{dC_3} \) | \( \omega \geq 9 \frac{\kappa_{23}}{dC_3} \) |
| \( L_z \) vs. \( d_3 \) | \( L_z/d_3 \geq 4.24 \) | \( 0.47 < L_z/d_3 < 4.24 \) | \( L_z/d_3 \leq 0.47 \) |
| \( n \) | \( q_3 d_3 \) | \( \tanh(q_3 d_3) \) | \( 1/\sqrt{\omega\kappa_{23}C_3} \) |
| \( n/\gamma_3 \) | \( d_3/\kappa_{23} \) | \( \tanh(d_3\sqrt{\omega\kappa_{23}C_3}/\sqrt{\omega\kappa_{23}C_3}) \) | \( \sqrt{\omega\kappa_{23}C_3} \) |
| \( \gamma_3 n \) | \( i\omega d_3 C_3 \) | \( \tanh(d_3\sqrt{\omega\kappa_{23}C_3}/\sqrt{\omega\kappa_{23}C_3}) \) | \( \sqrt{\omega\kappa_{23}C_3} \) |
| Thermal property | \( d_3\kappa_{23}, C_3 \) | \( \kappa_{23}/C_3, \sqrt{\kappa_{23}C_3} \) | \( \sqrt{\kappa_{23}C_3} \) |
The thermal effusivity depends strongly on the heat capacity input. A further calculation finds that the thermal effusivity \( \sqrt{\kappa z C_z} \) for multiple pairs of \( \kappa z \) and \( C_z \) is a constant at a frequency of 6.8 MHz. When the modulation frequency changes to 0.98 MHz and 6.8 MHz, the \( \kappa z - C_z \) pairs deviate from the values at 6.8 MHz. The \( \kappa z - C_z \) curves of the three modulation frequencies on the \( \kappa z - C_z \) diagram cross at 140 W/m K and 1.59 J/cm³ K for thermal conductivity and volumetric heat capacity for bulk Si at room temperature, which agree very well (within 5%) with the literature values, as shown in Fig. 2(c).

### B. SiO₂ thin films

Three SiO₂ thin films samples with the thickness of 110 nm, 310 nm, and 860 nm were grown by thermal oxidation at 1100 °C on a 350 µm thick Si wafer (same batch of wafers used in Sec. III A). Similarly, a 100 nm Al film was coated on the SiO₂ thin film samples by thermal evaporation to form the tri-layer configuration for thermal property measurements. The radii of pump and probe beam were selected as 15 µm and 5 µm, respectively, which results in the cross-plane thermal conductivity measurement of the thin films as shown in Eqs. (18b) and (14b).

For the 110 nm thick SiO₂ film sample, thermal resistance and heat capacity dominate the thermal response when the modulation frequency is lower than 1.18 MHz, calculated from Eq. (14b). At those frequencies below 1.18 MHz, the thermal waves penetrate throughout the SiO₂ layer and this layer can be only treated as an interface for data reduction of TDTR measurement, where the interfacial thermal conductances \( G_2 \) and \( G_4 \) cannot be separated from the thermal resistance of the thin film layer. At modulation frequencies much higher than 1.18 MHz, the measured signal is insensitive to \( G_2 \) and \( G_4 \) compared to the low conductance of thin film layer. Figure 3(a) shows the measurement data and best-fit results of \(-V_{in}/V_{out}\) for the 110 nm thick SiO₂ film with modulation frequencies of 0.5 MHz, 0.98 MHz, and 6.8 MHz. Figure 3(b) shows the \( \kappa z - C_z \) diagram. At 0.5 MHz and 0.98 MHz, the best-fit values of \( \kappa z \) are independent of \( C_z \), which indicates the thermal resistance \( d_3/\kappa z \) dominates the measured signals. At a higher frequency such as 6.8 MHz, the fitted thermal conductivity \( \kappa z \) increases with the fitted volumetric heat capacity \( C_z \), which indicates that thermal diffusivity \( \kappa z/C_z \) dominates in the signal. The \( \kappa z - C_z \) curves of the three modulation frequencies on the \( \kappa z - C_z \) diagram cross at 1.3 W/m K and 1.61 J/cm³ K for the thermal conductivity and volumetric heat capacity, respectively, for the 110 nm thick SiO₂ thin film.

For the 860 nm thick SiO₂ film sample, the \( \kappa z - C_z \) diagram can be constructed over 0.1–20 MHz since we found that the measured signals are insensitive to the interfacial thermal conductances \( G_2 \) and \( G_4 \) at these frequencies. Thermal effusivity dominates the thermal response when the modulation frequency is higher than 1.58 MHz for the 860 nm thick SiO₂ film sample, calculated from Eq. (18b), which is similar to the bulk Si measurement in Sec. III A. Figure 3(c) shows the measurement data and best-fit results of \(-V_{in}/V_{out}\) for the 860 nm thick SiO₂ film with modulation frequencies of 0.5 MHz, 2.08 MHz, 6.8 MHz, and 11.26 MHz. Figure 3(d) shows the \( \kappa z - C_z \) diagram where the \( \kappa z - C_z \) curves of the four modulation frequencies on the \( \kappa z - C_z \) diagram cross at 1.31 W/m K and 1.62 J/cm³ K for the thermal conductivity and volumetric heat capacity, respectively, for 860 nm thick SiO₂ thin film.

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**FIG. 2.** Demonstration of simultaneous measurement of thermal conductivity and volumetric heat capacity of bulk Si using frequency-dependent TDTR measurements. (a) The sensitivity of \(-V_{in}/V_{out}\) signal to the thermal conductivity \( \kappa z \) (solid line) and volumetric heat capacity \( C_z \) (dashed line) of bulk Si and the interfacial thermal conductance between Al and Si \( G_2 \) (dashed-dotted line) at 6.8 MHz. (b) The experiment data and best-fit results of \(-V_{in}/V_{out}\) under modulation frequencies of 0.5 MHz, 0.98 MHz, and 6.8 MHz. (c) The \( \kappa z - C_z \) diagram of bulk Si showing that multiple pairs of thermal conductivities \( \kappa z \) and volumetric heat capacity \( C_z \) can fit the measured signal under each modulation frequency. The crossing point of \( \kappa z \) for those three modulation frequencies is the measured value of the Si sample. The measured data agree very well (within 5%) with the reported values (open diamond) of bulk Si.
FIG. 3. Demonstration of simultaneous measurement of thermal conductivity and volumetric heat capacity of SiO$_2$ thin films using frequency-dependent TDTR measurements. (a) The experiment data and best-fit results of $-V_{in}/V_{out}$ for 110 nm thick SiO$_2$ film under modulation frequencies of 0.5 MHz, 0.98 MHz, and 6.8 MHz. (b) The $\kappa$-$C$ diagram for 110 nm thick SiO$_2$ film. The crossing point of $\kappa$-$C$ for those three modulation frequencies is the measured value of the sample. (c) The experiment data and best-fit results of $-V_{in}/V_{out}$ for 860 nm thick SiO$_2$ film under modulation frequencies of 0.5 MHz, 2.08 MHz, 6.8 MHz, and 11.26 MHz. (d) The $\kappa$-$C$ diagram for 860 nm thick SiO$_2$ film. (e) The sensitivity of $-V_{in}/V_{out}$ signal to the thermal conductivity $\kappa_{3}$ (solid line) and the heat capacity $C_{3}$ (dashed line) of 310 nm thick SiO$_2$ film and the interfacial thermal conductance $G_{4}$ (dashed-dotted line) from 0.98 MHz to 6.8 MHz at a 0.5 ns delay time. (f) The experiment data and best-fit results of $-V_{in}/V_{out}$ for 310 nm thick SiO$_2$ film under modulation frequencies of 0.98 MHz, 2.08 MHz, 3.4 MHz, and 6.8 MHz. (g) The $\kappa$-$C$ diagram of 310 nm thick SiO$_2$ film at 2.08 MHz, 3.4 MHz, and 6.8 MHz. (h) The measured values of thermal conductivity $\kappa_{3}$ and volumetric heat capacity $C_{3}$ for SiO$_2$ thin films with different thicknesses, which agree well with the reported values in the literatures.
Figure 3(e) shows the sensitivity of $-V_{in}/V_{out}$ signal to the thermal properties of the 310 nm thick SiO$_2$ film from 0.98 MHz to 6.8 MHz at a delay time of 0.5 ns. The $-V_{in}/V_{out}$ signal is insensitive to the interfacial thermal conductance $G_2$ at 2.08 MHz and above, where the $\kappa_{3}$ and $C_3$ can be extracted. Both thermal effusivity and thermal diffusivity play a role in the thermal response when the modulation frequency range is $0.15–12.15$ MHz for a 310 nm thick SiO$_2$ film sample, calculated from Eqs. (17b) and (18b). Figure 3(f) shows the experiment data and best-fit results for of $-V_{in}/V_{out}$ for the 310 nm thick SiO$_2$ thin film at 0.98 MHz, 2.08 MHz, 3.4 MHz, and 6.8 MHz. Figure 3(g) shows the $\kappa$-$C$ diagram of 2.08 MHz, 3.4 MHz, and 6.8 MHz. The $\kappa$-$C$ curves of these three modulation frequencies on the $\kappa$-$C$ diagram cross at 1.35 W/m K and 1.62 J/cm$^3$ K for the thermal conductivity and volumetric heat capacity, respectively, for the 310 nm thick SiO$_2$ thin film. The interfacial thermal conductance $G_2$ and $G_4$ for the 310 nm thick SiO$_2$ film are fitted at 0.98 MHz as 120 MW/m$^2$ K and 13 MW/m$^2$ K, respectively, which agree well with those reported values in Ref. 7.

Finally, Fig. 3(h) shows the measured values of thermal conductivity $\kappa$ and volumetric heat capacity $C$ for SiO$_2$ thin films with different thicknesses. Both $\kappa$ and $C$ do not change much with thickness, which indicates that the size effect of phonon transport is not important for SiO$_2$ at a thickness of 110 nm and above. This result agrees very well with the literature values.5,7

C. ALD/MLD-enabled thin film with unknown thermal properties

In Secs. III A and III B, we demonstrated the simultaneous measurement of both thermal conductivity and volumetric heat capacity of materials in both bulk and thin film forms using the frequency-dependent TDTR measurement, which can potentially shorten the development/discovery cycle of new materials. Here we apply this technique for measuring the thermal properties of a novel hybrid organic-inorganic multi-layer material enabled by ALD/MLD techniques. By utilizing the sequential self-limiting surface reactions to enable the atomic level layer-by-layer growth, ALD/MLD has recently emerged as a reliable conformal thin film deposition technique for novel nanostructured materials with tunable mechanical, electrical, and optical properties. The nature of such layer-by-layer nonequilibrium growth technique with atomic level control also has a great challenge in obtaining bulk samples for such novel materials, so that the conventional heat capacity measurement cannot be used to characterize such thin films. Here the frequency-dependent TDTR measurements were carried out using the tri-layer sample configuration at modulation frequencies of 0.5 MHz, 0.98 MHz, and 6.8 MHz to measure both volumetric heat capacity $C_3$ and thermal conductivity $\kappa_{3}$ of the ALD/MLD-enabled novel zincone thin films on a p-type 350 $\mu$m Si wafer. The zincone thin films with thicknesses of 193 nm and 380 nm were fabricated using diethylzinc and hydroquinone at 150 °C.

Figure 4(a) shows the experiment data and best-fit results of $-V_{in}/V_{out}$ for the 193 nm thick ALD/MLD-enabled zincone film at 300 K at three modulation frequencies of 0.5 MHz, 0.98 MHz, and 6.8 MHz for the 193 nm thick zincone thin film. The measured value of the sample. (b) The $κ$-$C$ diagram of the 193 nm thick zincone thin film. The crossing point of $\kappa$-$C$ under three modulation frequencies is the measured value of the sample. (c) The temperature-dependent volumetric heat capacity of 193 nm and 380 nm thick zincone thin films. (d) The temperature-dependent thermal conductivity of 193 nm and 380 nm thick zincone thin films.

FIG. 4. Simultaneous measurement of thermal conductivity and volumetric heat capacity of 193 nm and 380 nm thick ALD/MLD-enabled zincone thin films using frequency-dependent TDTR measurements. (a) The experiment data and best-fit results of $-V_{in}/V_{out}$ under 0.5 MHz, 0.98 MHz, and 6.8 MHz for the 193 nm thick zincone thin film. (Inset) The chemical composition of the zincone film. (b) The $κ$-$C$ diagram of the 193 nm thick zincone thin film. The crossing point of $\kappa$-$C$ under three modulation frequencies is the measured value of the sample. (c) The temperature-dependent volumetric heat capacity of 193 nm and 380 nm thick zincone thin films. (d) The temperature-dependent thermal conductivity of 193 nm and 380 nm thick zincone thin films.
0.5 MHz, 0.98 MHz, and 6.8 MHz with the inset showing the chemical composition of the zincone film. Figure 4(b) shows the \( \kappa-C \) diagram. The \( \kappa-C \) curves of the three modulation frequencies on the \( \kappa-C \) diagram cross at 0.147 W/m K and 2.95 J/cm\(^3\) K for the thermal conductivity and volumetric heat capacity, respectively. The measurement data are insensitive to both interfacial thermal conductance \( G_2 \) and \( G_4 \) because the thermal conductance of this thin film layer 0.76 MW/m\(^2\) K is two orders of magnitude lower than the interfacial thermal conductance of the two chemically bonded interfaces. Figures 4(c) and 4(d) show the temperature-dependent volumetric heat capacity and thermal conductivity of both 193 nm and 380 nm thick zincone thin films. Figure 4(c) shows that the volumetric heat capacity increases with temperature first and finally reaches a plateau at around 350 K. With the increasing temperature, more high frequency vibrational modes are excited, which leads to an increase in the heat capacity. At a temperature higher than the Debye temperature, the heat capacity reaches a plateau when all the vibration modes are excited. Despite the sample thickness difference, the heat capacity is almost the same for the two samples. Figure 4(d) shows that the thermal conductivity increases when the temperature increases from 150 K to 300 K because of the rapid increase of volumetric heat capacity and decreases with temperature due to the increased phonon-phonon scattering with increasing temperature. Different from heat capacity, the thermal conductivity shows a slight increase with thickness, which merits further investigation.

IV. CONCLUDING REMARKS

In this paper, we have described and validated a technique to simultaneously measure the thermal conductivity \( \kappa \) and volumetric heat capacity \( C \) of both bulk and thin film materials using frequency-dependent TDTR method. The heat transfer model is analyzed first to find how different combinations of \( \kappa \) and \( C \) determine the frequency-dependent TDTR signals. A "\( \kappa-C \)" diagram is proposed to determine thermal conductivity and heat capacity of the measured material using frequency-dependent TDTR signals. The technique is validated by measuring the thermal properties of bulk Si and SiO\(_2\) thin film samples and then extended to measure both \( \kappa \) and \( C \) of a novel ALD/MLD-enabled zincone thin film materials. This method is applicable to a large variety of bulk and thin film materials for simultaneous measurement of thermal conductivity and volumetric heat capacity, which can significantly shorten the material discovery cycle.

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APPENDIX: FREQUENCY-DOMAIN RESPONSE OF THE SURFACE TEMPERATURE CHANGE

We present here in detail the calculation of the frequency-domain response of the surface temperature change in the real space, which is obtained by solving the heat conduction equation for a Gaussian heat source on a multiple layer of materials and weighting the temperature distribution at the top surface by the Gaussian intensity distribution of the probe beam. Similar calculations can also be found in the literature.\(^7\,^9\,^{26}\)

Single layer and interface

Considering a cylindrical heating spot on the metallic transducer, which absorbs laser heating, the heat conduction equation can be written as the following for each layer:

\[
\frac{\kappa_r}{r} \frac{\partial}{\partial r} \left[ r \frac{\partial \tilde{\theta}(r, z)}{\partial r} \right] + \kappa_z \frac{\partial^2 \tilde{\theta}(r, z)}{\partial z^2} = C \frac{\partial \tilde{\theta}(r, z)}{\partial t},
\]

(A1)

where \( r \) is the radial coordinate, \( z \) is the cross-plane coordinate (in the depth direction), \( t \) is time, \( \tilde{\theta} \) is the temperature, \( C \) is the volumetric heat capacity, and \( \kappa_r \) and \( \kappa_z \) are the in-plane and cross-plane thermal conductivity, respectively.

To solve the equation with radial symmetry, the zeroth-order Hankel transform is performed to simplify Eq. (A1), which yields\(^15\)

\[
-\kappa_r x^2 \theta(z) + \kappa_z \frac{\partial^2 \theta(z)}{\partial z^2} = C \frac{\partial \theta(z)}{\partial t},
\]

(A2)

where \( x \) is the transform variable, and \( \theta \) is the temperature in Hankel transform. In the thermoreflectance measurement, the heating pulses are modulated by a frequency \( \omega_0 \) and the response are extracted from the probe laser beam at the frequency \( \omega_0 \) by a lock-in amplifier, so a solution of Eq. (A2) is sought in the frequency domain:

\[
\theta = u \exp[i(\omega t - \xi)],
\]

(A3)

where \( u \) is a function of \( z \) only, and \( \xi \) is an arbitrary constant. Substituting Eq. (A3) into Eq. (A2), we have

\[
\frac{\partial^2 \theta(\omega, z)}{\partial z^2} = q^2 \theta(\omega, z),
\]

(A4)

where

\[
q = \sqrt{\frac{\kappa_r x^2 + iC \omega}{\kappa_z}}.
\]

(A5)

The general solution of Eq. (A4) is

\[
\theta(z) = \alpha \exp(qz) + \beta \exp(-qz),
\]

(A6)

\[
F(z) = -\alpha \kappa_r q \exp(qz) + \beta \kappa_z q \exp(-qz),
\]

(A7)

where \( \alpha \) and \( \beta \) are constants, and \( \theta(z) \) and \( F(z) \) are the temperature and heat flux at the point \( z \). Let \( \theta \) and \( F \) be the temperature and heat flux at the face \( z = 0 \) and let \( \theta' \) and \( F' \) be their values at the face \( z = d \). The relation between these four quantities \( \theta, F, \theta', \) and \( F' \) can be expressed as

\[
\begin{bmatrix}
\theta' \\
F'
\end{bmatrix} = \begin{bmatrix}
A & B \\
C & D
\end{bmatrix} \begin{bmatrix}
\theta \\
F
\end{bmatrix}.
\]

(A8)
By substituting Eqs. (A6) and (A7) into Eq. (A8), \( \alpha \) and \( \beta \) can be eliminated, and we can easily get
\[
\hat{A} = \hat{B} = \cosh(qd), \quad \hat{B} = -\sinh(qd)/(\kappa_d q), \quad (A9)
\]
\[
\hat{C} = -\kappa_d q \sinh(qd).
\]

When heat diffuses through an interface, there should be a temperature difference between its two sides, and the only necessary property is the interface thermal conductance \( G \), which could be defined by
\[
F = F' = G(\theta - \theta'). \quad (A10)
\]
In matrix form Eq. (A10) will become
\[
\begin{bmatrix} \theta' \\ F' \end{bmatrix} = \begin{bmatrix} 1 & -1/G \\ 0 & 1 \end{bmatrix} \begin{bmatrix} \theta \\ F \end{bmatrix}, \quad (A11)
\]

Equations (A8) and (A11) are the heat transfer solutions for a single layer with thickness of \( d \) and an interface, respectively.

**Multilayer**

In a multilayer structure with \( n \) parallel layers inside,\(^17\) the temperature \( \theta_{j+1} \) and heat flux \( F_{j+1} \) on the bottom side of the \( j \)th layer should be the product of the temperature \( \theta_j \) and heat flux \( F_j \) on the top side with a matrix \( M_j \), i.e.,
\[
\begin{bmatrix} \theta_{j+1} \\ F_{j+1} \end{bmatrix} = \begin{bmatrix} A_j^+ & B_j^+ \\ C_j^+ & D_j^+ \end{bmatrix} \begin{bmatrix} \theta_j \\ F_j \end{bmatrix} = M_j \begin{bmatrix} \theta_j \\ F_j \end{bmatrix}. \quad (A12)
\]

Multiple layers are handled by multiplying the matrices for each individual layers in sequence. Therefore, the temperature \( \theta_{n+1} \) and heat flux \( F_{n+1} \) of the bottom side of the multilayer stack can be expressed by
\[
\begin{bmatrix} \theta_{n+1} \\ F_{n+1} \end{bmatrix} = \begin{bmatrix} A^+ & B^+ \\ C^+ & D^+ \end{bmatrix} \begin{bmatrix} \theta_1 \\ F_1 \end{bmatrix}, \quad (A13)
\]
where
\[
\begin{bmatrix} A^+ & B^+ \\ C^+ & D^+ \end{bmatrix} = M_n M_{n-1} \ldots M_1, \quad (A14)
\]

and \( \theta_1 \) and \( F_1 \) are the temperature and heat flux on the top side of the multilayer stack. If the heat flux is applied to the top surface of the first layer, and the \( n \)th layer is assumed to be semi-infinite or adiabatic, which means \( F_{n+1} = 0 \), the top surface temperature will be given as
\[
\theta_1 = -\frac{D^+}{C^+} F_1, \quad (A15)
\]
from Eq. (A13), where \( C^+ \) and \( D^+ \) are calculated via Eq. (A14).

**Frequency-domain response of surface temperature change**

The pump pulse heats the top surface and gives the top boundary condition as the cylindrical heat flux distribution
\[
\hat{I}_{\text{pump}}(r) = \frac{2 Q_{\text{pump}}}{\pi R_{\text{pump}}^2} \exp \left( -\frac{2r^2}{R_{\text{pump}}^2} \right), \quad (A16)
\]
which after taking the Hankel transform will give
\[
F_1(x) = I_{\text{pump}}(x) = \frac{Q_{\text{pump}}}{2\pi} \exp \left( -\frac{x^2 R_{\text{pump}}^2}{8} \right). \quad (A17)
\]
where \( Q_{\text{pump}} \) is the power absorbed from pump laser, and \( R_{\text{pump}} \) is the 1/e\(^2\) radius of pump intensity distribution as a Gaussian spot. Inserting Eq. (A17) to Eq. (A15) yields the surface temperature
\[
\theta_1(x) = -\frac{D^+}{C^+} \frac{Q_{\text{pump}}}{2\pi} \exp \left( -\frac{x^2 R_{\text{pump}}^2}{8} \right). \quad (A18)
\]
The surface temperatures are measured by thermoreflectance, i.e., the change in the reflectivity, which depends on the temperature change. This change in reflectivity is measured by changes in the reflected intensity of a probe laser beam. Let \( Q_{\text{probe}} \) be the power of probe beam and let \( R_{\text{probe}} \) be the 1/e\(^2\) radius of probe intensity distribution as a Gaussian spot. The thermoreflectance response \( H(x) \) contained in reflected probe beam should be the product of surface temperature \( \theta_1 \) and thermoreflectance coefficient \( \nu \), and weighted by the probe intensity distribution, considering the cylindrical spreading effects,\(^20\)
\[
H(x) = \nu \frac{Q_{\text{probe}}}{2\pi} \exp \left( -\frac{x^2 R_{\text{probe}}^2}{8} \right) \theta_1(x)
\]
\[
= -\nu \left( \frac{D^+}{C^+} \right) \frac{Q_{\text{pump}} Q_{\text{probe}}}{4\pi^2} \exp \left[ -\frac{x^2 (R_{\text{pump}}^2 + R_{\text{probe}}^2)}{8} \right]. \quad (A19)
\]
The frequency-domain response \( H(\omega) \) of the surface temperature change in real space can then be found by taking the inverse Hankel transform of Eq. (A19):
\[
H(\omega) = \nu \frac{Q_{\text{pump}} Q_{\text{probe}}}{2\pi} \int_0^\infty \left( \frac{D^+}{C^+} \right) \exp \left[ -\frac{x^2 (R_{\text{pump}}^2 + R_{\text{probe}}^2)}{8} \right] dx. \quad (A20)
\]

References: