elliptical-beam method shows the advantages of better accuracy and smaller measurement uncertainty.

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APPENDIX A: THERMAL MODEL FOR TDTR EXPERIMENTS ON ANISOTROPIC MATERIALS USING CIRCULAR OR ELLIPTICAL LASER SPOTS WITH OR WITHOUT BEAM OFFSET

The thermal transport model for the conventional TDTR experiments has been well established.[30,32] Here, we present a generally applicable thermal transport model that applies to the conventional TDTR experiments as well as the beam-offset TDTR experiments and the elliptical-beam TDTR experiments. In this model, when the beam spot sizes $w_x = w_y$ and offset distance $x_c \neq 0$, the model applies to the beam-offset case. When $w_x \neq w_y$ and $x_c = 0$, it applies to the elliptical-beam case. When $w_x = w_y$ and $x_c = 0$, it reduces to the conventional TDTR case.

We first start from the heat diffusion in a multilayered system with anisotropic thermal conductivity in each layer:

$$C\frac{\partial T}{\partial t} = K_x\frac{\partial^2 T}{\partial x^2} + K_y\frac{\partial^2 T}{\partial y^2} + K_z\frac{\partial^2 T}{\partial z^2} + 2K_{xy}\frac{\partial^2 T}{\partial x\partial y} + +2K_{xz}\frac{\partial^2 T}{\partial x\partial z} + +2K_{yz}\frac{\partial^2 T}{\partial y\partial z} \qquad \text{(A1)}$$

This parabolic partial differential equation can be simplified by doing Fourier transforms with respect to the in-plane coordinates and time, $T(x, y, z, t) \leftrightarrow \Theta(u, v, z, \omega)$, utilizing the following relationships

$$\mathcal{F}\{f(x)\} = F(u) = \int_{-\infty}^{\infty} f(x)e^{-i2\pi}ux\,dx$$

$$\mathcal{F}\left\{\frac{df(x)}{dx}\right\} = i2\pi uF(u)$$

$$\mathcal{F}\left\{\frac{d^2 f(x)}{dx^2}\right\} = -(2\pi u)^2 F(u)$$

as

$$(iC\omega)\Theta = -4\pi^2\big(K_x u^2 + 2K_{xy}uv + K_y v^2\big)\Theta + 2i2\pi\big(K_{xz}u + K_{yz}v\big)\frac{\partial\Theta}{\partial z} + K_z\frac{\partial^2\Theta}{\partial z^2} \quad \text{(A2)}$$

or more compactly,

$$\frac{\partial^2\Theta}{\partial z^2} + \lambda_2\frac{\partial\Theta}{\partial z} - \lambda_1\Theta = 0 \quad \text{(A3)}$$

where

$$\lambda_1 \equiv \frac{iC\omega}{K_z} + \frac{4\pi^2(K_x u^2 + 2K_{xy}uv + K_y v^2)}{K_z} \quad \text{(A4)}$$

$$\lambda_2 \equiv i4\pi\frac{K_{xz}u + K_{yz}v}{K_z} \quad \text{(A5)}$$

The general solution of Eq. (A3) is

$$\Theta = e^{u^+z}B^+ + e^{u^-z}B^- \quad \text{(A6)}$$

where u^+, u^- are the roots of the equation $x^2 + \lambda_2 x - \lambda_1 = 0$:

$$u^\pm = \frac{-\lambda_2 \pm \sqrt{(\lambda_2)^2 + 4\lambda_1}}{2} \quad \text{(A7)}$$

and B^+, B^- are the complex numbers to be determined.

From the Fourier's law of heat conduction $Q = -K_z(d\Theta/dz)$ and Eq. (A6), the heat flux can be expressed as:

$$Q = -K_z u^+ e^{u^+z}B^+ - K_z u^- e^{u^-z}B^- \quad \text{(A8)}$$

It is convenient to rewrite Eqs. (A6) and (A8) in matrices as

$$\begin{bmatrix}\Theta\\ Q\end{bmatrix}_{n,z} = [N]_n\begin{bmatrix}B^+\\ B^-\end{bmatrix}_n \quad \text{(A9)}$$

$$[N]_n = \begin{bmatrix} 1 & 1 \\ -K_z u^+ & -K_z u^- \end{bmatrix} \begin{bmatrix} e^{u^+ z} & 0 \\ 0 & e^{u^- z} \end{bmatrix}_n \tag{A10}$$

where *n* stands for the *n*-th layer of the multilayer system, and *z* is the distance within the *n*-th layer from its surface.

The constants B^+, B^- for the *n*-th layer can also be obtained from the surface temperature and heat flux of that layer by setting z = 0 in Eq. (A10) and calculating the inverse matrix of Eq. (A9) as:

$$\begin{bmatrix} B^+ \\ B^- \end{bmatrix}_n = [M]_n \begin{bmatrix} \Theta \\ Q \end{bmatrix}_{n,z=0} \tag{A11}$$

$$[M]_n = \frac{1}{K_z(u^+ - u^-)} \begin{bmatrix} -K_z u^- & -1 \\ K_z u^+ & 1 \end{bmatrix} \tag{A12}$$

For heat flow across the interface, the heat flux and the temperature can be expressed as

$$Q_{n,z=L} = Q_{n+1,z=0} = G(\Theta_{n,z=L} - \Theta_{n+1,z=0}) \tag{A13}$$

$$\Theta_{n+1,z=0} = \Theta_{n,z=L} - \frac{1}{G} Q_{n,z=L} \tag{A14}$$

where *G* is the interface thermal conductance. It is convenient to rewrite Eqs. (A13) and (A14) in matrices as

$$\begin{bmatrix} \Theta \\ Q \end{bmatrix}_{n+1,z=0} = [R]_n \begin{bmatrix} \Theta \\ Q \end{bmatrix}_{n,z=L} \tag{A15}$$

$$[R]_n = \begin{bmatrix} 1 & -1/G \\ 0 & 1 \end{bmatrix} \tag{A16}$$

The temperature and heat flux on the surface of the first layer can thus be related to those at the bottom of the substrate as

$$\begin{bmatrix} \Theta \\ Q \end{bmatrix}_{n,z=L_n} = [N]_n [M]_n \cdots [R]_1 [N]_1 [M]_1 \begin{bmatrix} \Theta \\ Q \end{bmatrix}_{1,z=0} = \begin{bmatrix} A & B \\ C & D \end{bmatrix} \begin{bmatrix} \Theta \\ Q \end{bmatrix}_{1,z=0} \tag{A17}$$

Applying the boundary condition that the heat flux at the bottom of the substrate is zero, there is $0 = C\Theta_1 + DQ_1$. The temperature response function H, which is the detected temperature change in response to the applied heat flux, can thus be found out as

$$H(u, v, \omega) = \frac{\Theta_1}{Q_1} = -\frac{D}{C} \tag{A18}$$

The next step is to simulate the heating and signal detection in TDTR experiments. The sample surface is heated by an elliptical pump beam that has a Gaussian distribution of intensity $p_0(x, y)$ expressed as

$$p_0(x, y) = \frac{2A_0}{\pi\sigma_{x_0}\sigma_{y_0}} \exp\left(-\frac{2x^2}{\sigma_{x_0}^2}\right) \exp\left(-\frac{2y^2}{\sigma_{y_0}^2}\right) \tag{A19}$$

where σ_{x_0} and σ_{y_0} are the $1/e^2$ radii of the pump spot in the x and y directions respectively. The 2-D Fourier transform of $p_0(x, y)$ utilizing the following relationships

$$\mathcal{F}\{f(x, y)\} = F(u, v) = \iint f(x, y) e^{-i2\pi(ux+vy)} dxdy$$

$$\mathcal{F}\left\{e^{-ax^2}\right\} = \int_{-\infty}^{\infty} e^{-ax^2} \, e^{-i2\pi ux} dx = \sqrt{\left(\frac{\pi}{a}\right)} \, e^{-\pi^2 u^2/a}$$

yields

$$P_0(u, v) = A_0 \exp\left(-\frac{\pi^2 u^2 \sigma_{x_0}^2}{2}\right) \exp\left(-\frac{\pi^2 v^2 \sigma_{y_0}^2}{2}\right) \tag{A20}$$

The distribution of surface temperature oscillation is the inverse transform of the product of the heat flux $P_0(u, v)$ and the temperature response function $H(u, v)$

$$\theta(x, y) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P_0(u, v) H(u, v) e^{i2\pi(ux+vy)} dudv \tag{A21}$$

The surface temperature oscillation is measured as a weighted average by an elliptical probe beam with x- and y-offsets to the pump as

$$\Delta T = \frac{2}{\pi \sigma_{x_1} \sigma_{y_1}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \theta(x,y) \exp\left(-\frac{2(x-x_c)^2}{\sigma_{x_1}^2}\right) \exp\left(-\frac{2(y-y_c)^2}{\sigma_{y_1}^2}\right) dxdy \qquad \text{(A22)}$$

where σ_{x_1} and σ_{y_1} are the $1/e^2$ radii of the probe spot in the *x* and *y* directions, respectively, and x_c and y_c are the offset distance between the pump and the probe in the *x* and *y* directions, respectively.

The integral of θ over *x* and *y* in Eq. (A22) is the inverse Fourier transform of the probe beam, leaving an integral over *u* and *v* that must be evaluated numerically

$$\Delta T = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} H(u,v) \exp(-\pi^2 u^2 w_x^2) \exp\left(-\pi^2 v^2 w_y^2\right) \exp\left(i2\pi(ux_c + vy_c)\right) dudv \qquad \text{(A23)}$$

where $w_x^2 = (\sigma_{x_0}^2 + \sigma_{x_1}^2)/2$, $w_y^2 = (\sigma_{y_0}^2 + \sigma_{y_1}^2)/2$.

The signal detected by the lock-in amplifier is[37]

$$\Delta R_M(\omega_0) = \frac{dR}{dT} \sum_{n=-\infty}^{\infty} \Delta T(\omega_0 + n\omega_s) e^{in\omega_s t_d} \qquad \text{(A24)}$$

where ω_0 is the modulation frequency of pump heating, ω_s is the sampling frequency by the laser pulses (i.e., 2π times the laser repetition rate), t_d is the delay time between pump and probe, and dR/dT is the thermoreflectance coefficient. More specifically, lock-in amplifier will have in-phase and out-of-phase outputs which are the real and imaginary parts of ΔR_M respectively:

$$V_{in} = \mathrm{Re}\{\Delta R_M(\omega_0)\} = \frac{1}{2}\frac{dR}{dT} \sum_{n=-\infty}^{\infty} [\Delta T(\omega_0 + n\omega_s) + \Delta T(-\omega_0 + n\omega_s)] e^{in\omega_s t_d} \qquad \text{(A25)}$$

$$V_{out} = \mathrm{Im}\{\Delta R_M(\omega_0)\} = -\frac{i}{2}\frac{dR}{dT} \sum_{n=-\infty}^{\infty} [\Delta T(\omega_0 + n\omega_s) - \Delta T(-\omega_0 + n\omega_s)] e^{in\omega_s t_d} \qquad \text{(A26)}$$

The ratio $R = -V_{in}/V_{out}$ a function of delay time t_d is usually taken as the signal to extract the unknown thermal properties by comparing the thermal model calculations to the measurements.