Thermal wave propagation in thin films on substrates

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A simple dispersion equation for surface thermal waves propagating along a solid surface covered with a thin film of higher thermal conductivity is presented. It is shown to describe well phase measurements with a photothermal microscope carried out on metal films on glass substrates. © 1995 American Institute of Physics.

I. INTRODUCTION

The evaluation of the thermal properties of thin films is a problem of great importance,[1,2] and recently there has been growing interest in this area in application to diamond films.[3] Among the techniques for thermal measurements at solid surfaces, thermal waves generated and detected optically have attracted great interest.[4-6] A classical thermal wave method for thermal diffusivity measurements[7] is based on a simple dispersion relation for harmonic heat diffusion waves in a homogeneous isotropic solid:

$$q^2 = i\omega/\kappa, \tag{1}$$

where κ is the thermal diffusivity, ω and q are the angular frequency and the wave number, with the temperature field in a one-dimensional wave having an appearance $T \propto \exp(iqx - i\omega t)$. Thus, it is straightforward to obtain the thermal diffusivity by measuring the phase lag in the thermal wave[7] $\Delta\theta = (\omega/2\kappa)^{1/2}\Delta x$. A modern version of this phase lag technique for photothermal microscopy at surfaces is described in Ref. 8, where the phase of a thermal wave, excited by a focused modulated laser beam and propagating along the surface, is measured with a probe beam via modulated reflectance.[9] Recently thermal wave phase measurements have been applied to free-standing diamond films[10] as well as to thin metal and diamond films on substrates.[11]

The question that the present report deals with is how the dispersion relation (1) for thermal waves propagating along the surface should be modified for a thin film on a substrate. We consider the film to be "thermally thin", i.e., thin compared to the characteristic thermal diffusion length

$$h \ll L_f = (2\kappa_f/\omega)^{1/2}, \tag{2}$$

where h is the film thickness and κ_f is the film thermal diffusivity. One can expect that a film much thinner than the thermal wavelength would have no substantial influence on the thermal wave propagation. It is not the case, however, when a film with high conductivity on a poorly conducting substrate is involved. Indeed, micron-thick metal films on glass substrates appear to affect the heat propagation at frequencies of the order of kHz when L_f is close to 1 mm.[11] Note that frequencies currently used in photothermal microscopy[5,8,12] as well as in other harmonic thermal wave techniques[4,6,10] do not usually exceed 1 MHz, providing thus

$L_f \geq 6$ μm for a typical value $\kappa_f \sim 1$ cm²/s, so that the model of a thermally thin film is quite reasonable for sub-micron metal or diamond films. Here we present a simple dispersion equation for this case and prove it with thermal wave phase measurements on thin gold films.

II. RESULTS AND DISCUSSION

We consider a substrate occupying a half-space $z > 0$ with a film of thickness h on it. Heat transport in the substrate is described by the heat diffusion equation

$$\frac{\partial T}{\partial t} = \kappa_s \nabla^2 T, \tag{3}$$

where κ_s is the thermal diffusivity of the substrate. For the film being thermally thin, its temperature is assumed to be uniform over the film thickness and equal to the substrate temperature at $z = 0$. The heat transport equation for the film incorporating heat exchange with the substrate can then be written as

$$\sigma \frac{\partial T}{\partial t} = \sigma\kappa_f \nabla_\perp^2 T + \lambda_s \frac{\partial T}{\partial z}, \quad z = 0, \tag{4}$$

where σ is the specific heat per unit area of the film, $\sigma = \rho_f c_f h$ with ρ_f and c_f being the density and the specific heat in the film; $\nabla_\perp^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2$; λ_s is the substrate thermal conductivity. Thus, in the presence of a thin film a modified boundary condition (4) at $z = 0$ should be used instead of the ordinary free surface boundary condition $\partial T/\partial z = 0$. This result is also valid for a vertically inhomogeneous film, with an effective value of κ_f being used: $\kappa_f^{eff} = (1/\sigma)\int \rho_f c_f \kappa_f\, dz$, $\sigma = \int \rho_f c_f\, dz$.

By using for a thermal wave an ansatz $T = f(z) \times \exp(iqx - i\omega t)$ Eqs.(3)–(4) yield the simple result that

$$T = T_0 \exp(-\beta z)\exp(iqx - i\omega t),$$
$$\beta = (q^2 - i\omega/\kappa_s)^{1/2} \tag{5}$$

with q and ω being related by

$$i\omega/\kappa_f - q^2 = (\lambda_s/h\lambda_f)(q^2 - i\omega/\kappa_s)^{1/2}, \tag{6}$$

where $\lambda_{f,s} = \rho_{f,s}\, c_{f,s}\, \kappa_{f,s}$ is the thermal conductivity of the film or substrate, respectively. This is our new dispersion equation that Eq. (1) should be replaced with in the presence of a thin film. In an explicit form it can be written as follows:
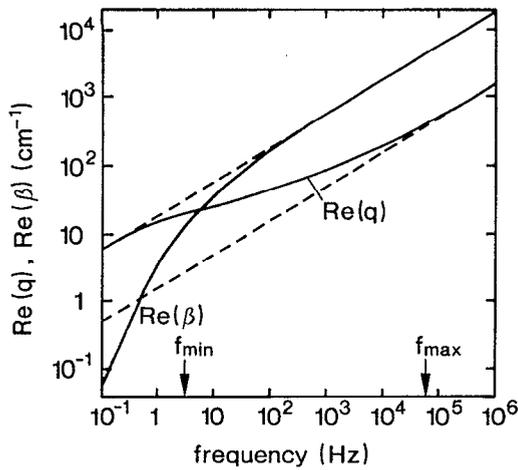
FIG. 1. Thermal wave dispersion curve (real part of the wave number vs frequency) for a 1-μm-thick gold film on fused silica. Also shown is the dispersion of Re(β), characterizing the penetration depth of the thermal wave into the substrate. Dashed lines show the dispersion curves for bulk gold (the lower curve) and silica (the upper one) according to Eq. (1).

$$q^2 = \frac{i\omega}{\kappa_f} + \frac{q_0^2}{2}\left[1 - \sqrt{1 - \frac{4i\omega}{\kappa_s q_0^2}(1 - \kappa_s/\kappa_f)}\right], \qquad (7)$$

where $q_0 = \lambda_s/h\lambda_f$.

It should be noted that the validity of the dispersion equation obtained does not depend on whether the film thermal conductivity is greater or smaller than that of the substrate. However, Eq. (4) and hence Eqs. (6)–(7) are valid only for a thermally thin film conforming to Eq. (2). Under this condition, one can easily see that Eq. (7) yields just a trivial result $q^2 \simeq i\omega/\kappa_s$, i.e., the thermal wave dispersion equation for the substrate material, unless λ_f is much larger than λ_s. That is, a thermally thin film substantially affects the thermal wave propagation only if being of much higher conductivity than the substrate. In this latter case there are two important characteristic frequencies:

$$\omega_{min} = q_0^2 \kappa_s, \qquad \omega_{max} = q_0^2 \kappa_f^2/\kappa_s = (\kappa_f/\kappa_s)^2 \omega_{min}.$$

If $\omega \ll \omega_{min}$ we get again a dispersion relation (1) with $\kappa = \kappa_s$, i.e., no coating effect. In the opposite limiting case $\omega \gg \omega_{max}$ we get Eq. (1) with $\kappa = \kappa_f$, i.e., for the film unaffected by the substrate. In this case the thermal diffusion length in the substrate is much less than the film thickness and the conditions of heat propagation are close to those for a free-standing film. Thus, the region where the thermal wave behavior is not trivial spreads nearly from ω_{min} to ω_{max}. Note that this region can be wide enough as the ratio ($\omega_{max}/\omega_{min}$) is, e.g., for a metal film on a glass substrate, of the order of 10^4.

Presented in Fig. 1 is the behavior of the real part of the wavenumber q against frequency f=$\omega/2\pi$ for a 1-μm-thick gold film on fused silica obtained with Eq. (7). One can see the asymptotic behavior at low and high frequencies to be in agreement with the above consideration. In the intermediate region $\omega_{min} \ll \omega \ll \omega_{max}$ the dispersion can be shown to be described by a simplified equation

$$q^2 = (i-1)q_0\sqrt{\frac{\omega}{2\kappa_s}} \qquad (8)$$

so that the wavenumber is proportional to $\omega^{1/4}$ instead of the usual $\omega^{1/2}$ dependence. Another interesting feature is that the imaginary part of q is larger than the real part in this region, which implies that the thermal wave becomes "more dissipative" compared to the usual thermal wave of Eq. (1): a phase lag of 1 rad corresponds to attenuation by a factor of $\exp[\tan(3\pi/4)] \simeq 11$ in contrast to the usual $1/e$ attenuation. The frequency dependence of the real part of β, characterizing the thermal wave attenuation with depth, is also shown in Fig. 1. For $\omega_{min} < \omega < \omega_{max}$ the thermal wave penetration depth into the substrate $[\mathrm{Re}(\beta)]^{-1}$ becomes smaller than the wavelength while remaining still larger than the film thickness, so in this region we really deal with a "surface thermal wave."

The dispersion equation (6) can also be obtained from the more strict consideration of a film of finite thickness. In this approach the temperature field in the film is also described by a bulk heat diffusion equation (3) with $\kappa = \kappa_f$ and the boundary conditions $T_f = T_s$, $\lambda_f \partial T_f/\partial z = \lambda_s \partial T_s/\partial z$ at the interface and $\partial T_f/\partial z = 0$ at the free surface are applied. The temperature field in the thermal wave propagating along the surface is then given by

$$T = T_0 \exp(iqx - i\omega t)$$

$$\times \left\{ \begin{array}{l} [\exp(-\beta_f z) + \exp(\beta_f z - 2\beta_f h)], \\ \quad \text{in the film,} \quad -h < z < 0 \\ 2[1 + (\lambda_s\beta/\lambda_f\beta_f)]^{-1}\exp(-\beta z), \\ \quad \text{in the substrate,} \quad z > 0 \end{array} \right\},$$

$$\beta = (q^2 - i\omega/\kappa_s)^{1/2}, \quad \beta_f = (q^2 - i\omega/\kappa_f)^{1/2},$$

with the dispersion relation

$$\cosh(\beta_f h) + \frac{\lambda_f \beta_f}{\lambda_s \beta} \sinh(\beta_f h) = 0. \qquad (9)$$

For a thermally thin film $\beta_f h \ll 1$, and taking $\cosh(\beta_f h) \cong 1$ and $\sinh(\beta_f h) \cong \beta_f h$ we come again to Eq. (6). In the instance of Fig. 1 where the condition for the film to be thermally thin holds well over the frequency region shown, Eq. (9) yields values of $Re(q)$ differing not more than by 0.05% from those obtained with Eq. (6).

In application to thermoreflectivity measurements in photothermal microscopy, Eq. (7) describes the phase slope of the surface temperature at large distances from the heating laser beam. We confirmed this fact by numerical calculations of the surface temperature profiles with exact solutions for the three-dimensional harmonic heat flow in a layered structure,[4,13] as well as by measurements carried out on thin gold films on glass substrates. As an example, Fig. 2 presents the phase profile of the surface temperature on a 1-μm-thick gold film on BK7 glass, that was heated by an argon ion laser beam modulated with 680 Hz frequency and focused into a Gaussian spot with an $1/e$ radius of 50 μm. The surface temperature was monitored via modulated reflectance with a probe beam of 5 μm waist radius. Also shown is a phase profile calculated numerically using formulae of Refs. 4 and
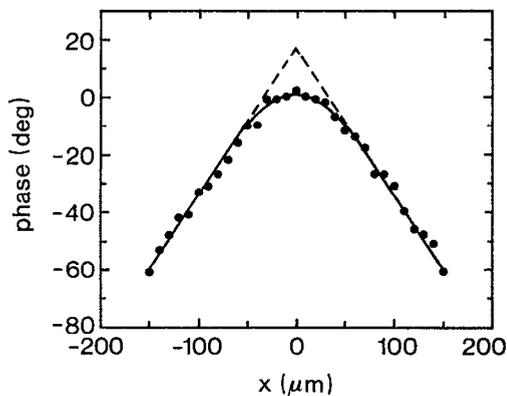
FIG. 2. Phase profile of the surface temperature for a 1-μm-thick electron beam evaporated gold film on BK7 glass at 680 Hz. Circles: measured data, solid curve: numerical simulation, dashed lines: $\Delta\theta = Re(q)\Delta x$, with q calculated with Eq. (7).

13, with the best fit yielding a film thermal diffusivity value $\kappa_f = 0.96$ cm^2/s. Note that the literature value for gold[14] is 1.28 cm^2/s and lower values were reported for thin gold films.[15] For the above value of κ_f Eq. (6) gives $Re(q) = 89$ cm^{-1}. One can see that a linear dependence $\Delta\theta = Re(q)\Delta x$ well describes the asymptotic behavior of the phase outside the pump laser spot.

Further measurements were carried out on a 0.5-μm-thick gold film with the modulation frequency varying from 15 to 3000 Hz and with both pump and probe beam spots having radii 15 μm. The phase of the surface temperature was measured at distances 50 to 200 μm from the pump beam and the real part of q was then determined from the slope of the $\theta(x)$ dependence. The measured dispersion curve presented in Fig. 3 follows nearly the $\omega^{1/4}$ − law. The data can be seen to be well described by a dispersion curve of Eq. (7), with a film thermal diffusivity value $\kappa_f = 1.02 \pm 0.04$ being obtained by the least-squares fit.
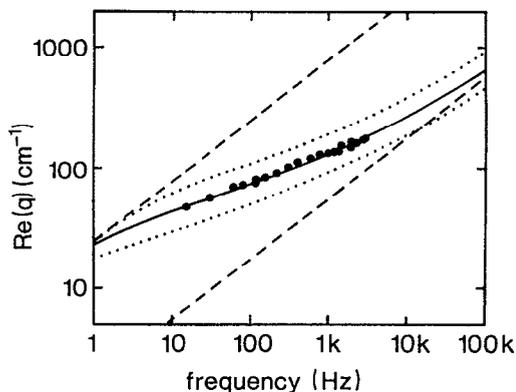

FIG. 3. Measured (circles) and calculated for $\kappa_f = 1$ cm^2/s (solid line) thermal wave dispersion curves for a 0.5-μm-thick electron beam evaporated gold film on a BK7 glass substrate. Dashed lines show the asymptotic behaviour of the calculated dispersion curve at low and high frequency limits. Dotted curves were calculated for $\kappa_f = 0.5$ cm^2/s (upper curve) and 2 cm^2/s (lower curve).

Thus, Eq. (7) can be used to obtain thin film thermal diffusivities from the asymptotic behavior of the phase of the surface temperature. In practice this means that the pump and probe beams should be separated by several beam radii. For example, in the case illustrated by Fig. 2, the phase slope obtained by Eq. (7) differs from the result of the exact theory less than by 0.5% at a distance x=100 μm (i.e., twice the beam radius) which would lead to an error of less than 1% in the film diffusivity.[16] We also note that if the thermal properties of the substrate are well defined, there is no need to measure the whole dispersion curve, as a measurement of the $Re(q)$ at any given frequency larger than f_{min} would suffice.

III. CONCLUSION

We have thus obtained a simple dispersion equation for thermal wave propagating along a solid surface covered with a thermally thin layer. Its potential for photothermal microscopy measurements is determined by the fact that at large distances from the heating laser spot the phase of the surface temperature is a linear function of distance with its slope being given by the dispersion equation. In comparison with the usage of the exact three-dimensional theory[4,5,13] to simulate numerically the amplitude and phase profiles of the surface temperature[11] this approach would have an advantage in that it avoids complicated calculations and depends neither on the heating beam profile nor on variations in the surface reflectivity.

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[16] See also Ref. 8 where Eq. (1) is shown to yield the same results as the exact three-dimensional theory for measurements on bulk samples with the experimental geometry similar to ours.