

Non-linear photothermal response of thin solid films and coatings

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Abstract

The analysis of the thermal-wave second-harmonic generation in thin films and coatings is presented. It is demonstrated theoretically that thicknesses much less than the thermal-wave penetration (diffusion) length may be measured from the detection of the second-harmonic thermal-wave phase variations. The theory developed describes the crucial dependence of the depth resolution of the resulting non-linear photothermal microscope on the material non-linear parameters.

1. Introduction

Significant interest in non-linear photothermal imaging was generated as a result of the first publications [1,2] on this topic. The basic idea is to modulate a heating laser beam at an angular frequency ω , but to detect the temperature variation of the sample at angular frequency 2ω . The generation of the second harmonic signal is caused by the dependence of the thermophysical parameters of matter on temperature [1-4]. It is important to use detection instrumentation with linear behavior to examine non-linear effects. In the initial non-linear experiments [1,2] the mirage-effect (or photothermal-optical beam deflection) detection technique was applied. The most important result was that, when the object was raster-scanned, harmonic images of cracks showed very high contrast when compared with the fundamental image. The recent experiments [3] with a thermal-wave imaging system based on gas-microphone detection of the second-harmonic component of the photoacoustic signal demonstrated that non-linear response also provides better contrast in depth-profiling applications.

For the analysis of the resolution of the non-linear thermal-wave microscope, a theoretical description of the second-harmonic generation in semi-infinite samples was proposed [4]. The dependences of heat capacity $C = C(T)$ and thermal conductivity $k = k(T)$ on temperature T were taken into account. It has been

argued [4] that there may be a significant gain in spatial resolution when applying detection at higher harmonics of the modulation frequency. Detection of the n th harmonics (i.e. at $\omega_n = n\omega$) gives a resolution equivalent to a linear detection scheme of modulation frequency $n^2\omega$.

In our theoretical analysis of non-linear photothermal phenomena we presented [5] a careful re-examination of thermal-wave second-harmonic generation in a semi-infinite spatial domain. The detailed description of variation with depth of the second-harmonic amplitude, $A_{2\omega}$, and phase, $\phi_{2\omega}$, was thus obtained. It was shown that the 2ω thermal wave (excited both by bulk and boundary non-linearities) consists, in general, of two components. The first component may be considered as *free-propagating*, because it satisfies the thermal-wave dispersion relation at frequency 2ω . If we denote the complex thermal-wave number at frequency ω as $p(\omega) = \sqrt{-i\omega/D_0}$, with D_0 being the equilibrium thermal diffusivity of the material, then the wave number of the free-propagating 2ω component will be $p(2\omega)$. The second component of the 2ω thermal wave may be considered as *forced*, because its space-time behavior is induced by the spatial distribution and the time dynamics of bulk second-harmonic sources, which are related to the square of the temperature field at the fundamental frequency. As the fundamental thermal-wave spatial distribution is governed by its wavenumber $p(\omega)$ (i.e. depends on $p(\omega)z$, where z is the coordinate), then the 2ω -forced component depth distribution is governed by $2p(\omega)z = p(2\omega)z$. This separation of the 2ω temperature field into two contributions provides a better understanding of the physical origin of the method and

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can be used as a guide to increase the resolution of the photothermal depth profiling proposed earlier [4]. According to those authors, one should operate with the forced component of the second-harmonic temperature field to achieve 2ω thermal wave attenuation closer to the laser-irradiated surface and the best spatial resolution of the photothermal microscope.

At the same time, the detailed analysis [5] revealed the crucial dependence of the spatial distribution of the second-harmonic amplitude and phase on the magnitude of the parameter $A \equiv (\delta_1 - 2\delta_3)/(\delta_2 - \delta_3)$ characterizing the non-linear photothermal process. Here $\delta_1 = (1/C)(\partial C/\partial T)$, $\delta_2 = (1/k)(\partial k/\partial T)$ and $\delta_3 = (1-R)^{-1}(\partial R/\partial T)$. The formal origin for this phenomenon is the proportionality of the free-propagating and forced components of the 2ω thermal wave to different combinations of the parameters δ_1 , δ_2 and δ_3 (i.e. to $(\delta_1 - \delta_2 - \delta_3)$ and to $(\delta_1 - 2\delta_2)$, respectively). As a result, the interference pattern formed by free-propagating and forced 2ω thermal waves is extremely sensitive to the magnitude and the sign of the dimensionless parameter A . It was demonstrated [5] that, depending on the magnitude of A , the maximum amplitude of the second-harmonic thermal wave may be realized at the surface or in the bulk of the crystal. The local 2ω temperature minimum (besides the one at $z \rightarrow \infty$) may also be localized at $z = 0$ or near the laser-irradiated surface. There is no 2ω signal at the surface ($z = 0$) for the critical value of the characteristic parameter $A = A_{cr} \equiv -\sqrt{2}$.

The most important result was the demonstration that for some parameters A the combined spatial 2ω temperature gradients are even steeper than in the pure forced 2ω wave. This, for example, was shown [5] for $|A| \ll 1$, typical of semiconductors exhibiting only weak dependence of reflectivity on temperature. Thus, the theoretical analysis [5] predicted that in some specific materials, or through specific choices of the laser optical frequency to minimize A (as the reflectivity depends on the optical energy quantum), the spatial resolution of non-linear photothermal imaging may be improved beyond the limit estimated previously [4]. In particular, enhanced sub-surface spatial resolution may result with materials in which the dominant role of the non-linearity is associated with the dependence of the thermal conductivity on temperature. The recent theory [5] made the connection between the physical nature of this effect and the observation that non-linearities associated with heat capacity and reflectivity dependences on temperature may operate even under spatially homogeneous conditions, while the non-linearity associated with $k = k(T)$ appears only in the regions with a spatially varying temperature field. The latter kind of non-linearity may provide a spatial contrast to the 2ω temperature field in addition to that

generated by the two former non-linearities. From this point of view the 2ω temperature field generation can also be treated as a result of the competition between different mechanisms of second-harmonic generation owing to $(\partial k/\partial T)$, $(\partial C/\partial T)$ and $(\partial R/\partial T)$, which are not phase-synchronized.

In order to extend our theoretical prediction that steeper 2ω temperature-field spatial gradients in a semi-infinite sample are equivalent to increased resolution in depth profiling, in the present paper we have examined the thermal-wave second-harmonic excitation both in a free-standing film and in a film resting on a backing. The analytical description obtained demonstrates explicitly the enhanced spatial resolution of non-linear photothermal depth profilometry. At the same time, the results presented below contribute to better physical insight into the non-linear photothermal wave phenomena as a whole.

2. Theory

Let us first re-examine the basic mathematical formalism for the description of the thermal-wave second-harmonic excitation [4,5] in the specific case of 1-D layered structures. We will start from the well-established form of the heat conduction equation, taking into account the possible temperature variation of heat capacity and thermal conductivity [6]:

$$C \frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) \quad (1)$$

Here $C = \rho C_p$ with ρ denoting the density of the material and C_p the specific heat at constant pressure. In Eq. (1) we have neglected the thermal and acoustic wave coupling, considering the thermal conductivity to be subsonic. In other words, we have assumed the characteristic frequency ω to be much lower than the one at which the wave numbers of thermal and acoustic waves become equal:

$$\omega \ll \omega_D \equiv C_L^2/D_0$$

where C_L is the longitudinal sound velocity. We will describe the laser action by introducing the modulated heat flux boundary condition at the irradiated surface

$$k \frac{\partial T}{\partial z} \Big|_{z=0} = -(1-R)(I_0 + I_\omega \cos \omega t) \quad (2)$$

where I_0 and I_ω denote averaged and modulated components of light intensity, respectively. At the internal interfaces of the layered structure considered ($z = h_i > 0$, $i = 1, 2, \dots, m$, where m is the number of

interfaces) the boundary conditions are:

$$k \frac{\partial T}{\partial z} \Big|_{h_i+0} = 0, T|_{h_i+0} = 0 \quad (3)$$

Here we have used ± 0 spatial shifts to denote the temperature and heat flux functions at opposite sides of the interface.

In a manner similar to the semi-infinite homogeneous sample [5], the second harmonic of the thermal wave in the problem described by Eqs. (1)–(3) may be induced by the first-order corrections to the initial heat capacity, thermal conductivity and surface reflectivity:

$$C \approx C_0(1 + \delta_1 T_1) \quad k \approx k_0(1 + \delta_2 T_1) \\ 1 - R \approx (1 - R_0)(1 + \delta_3 T_1) \quad (4)$$

where $T_1 = T - T_0$ is the laser-induced temperature rise, T_0 is the initial temperature, $C_0 \equiv C(T_0)$, $k_0 \equiv k(T_0)$, $R_0 \equiv R(T_0)$, and $\delta_1, \delta_2, \delta_3$ are also evaluated at $T = T_0$. However, in the layered structure under examination there is, in principle, an additional source of second-harmonic generation related to interface h_i motion (i.e. layer “breathing”) caused by the material thermal expansion.

$$h_i = h_{i0} \left(1 + \frac{1}{h_{i0}} \sum_{j=1}^i \beta_j^* \int_{h_{(j-1)0}}^{h_{j0}} T_1(z) dz \right) \quad (5)$$

where $h_{j0} = h_j(T_0)$, β_j^* is the bulk thermal expansion coefficient of the j th layer effective in 1-D geometry

$$\beta_j^* = \beta_j [1 - (4/3)(C_{Tj}/C_{Lj})^2]$$

β is the ordinary bulk thermal expansion coefficient of elastically isotropic solids, and C_T is the velocity of transverse acoustic waves. Note that, according to the structure of Eq. (5) and in the sequel, we are measuring distances to the interfaces from the photothermally excited front surface. Under the condition

$$\frac{1}{h_{i0}} \left| \sum_{j=1}^i \beta_j^* \int_{h_{(j-1)0}}^{h_{j0}} T_1(z) dz \right| \ll 1$$

one can expand the functions T_1 and $\partial T_1/\partial z$ at the interfaces ($z = h_i$) in Taylor series. We will keep in these expansions only the first terms which may be responsible for the 2ω excitation:

$$T_1(h_i) \approx T_1(h_{i0}) + \frac{\partial T_1}{\partial z}(h_{i0}) \sum_{j=1}^i \beta_j^* \int_{h_{(j-1)0}}^{h_{j0}} T_1 dz \\ \frac{\partial T_1}{\partial z}(h_i) \approx \frac{\partial T_1}{\partial z}(h_{i0}) + \frac{\partial^2 T_1}{\partial z^2}(h_{i0}) \sum_{j=1}^i \beta_j^* \int_{h_{(j-1)0}}^{h_{j0}} T_1 dz \quad (6)$$

In the next step one can look for a solution of the problem (Eqs. (1)–(4),(6)) in the form:

$$T_1 = T_{10} + T_\omega + T_{2\omega} = \text{Re}\{T_{10} + \tilde{T}_\omega e^{-i\omega t} + \tilde{T}_{2\omega} e^{-2i\omega t}\} \quad (7)$$

Then, under the conditions of the stepwise successive approximation method [5], the description of the time-averaged temperature field, the fundamental thermal-wave component (T_ω), and the second-harmonic component ($T_{2\omega}$) may be separated out. To evaluate the 2ω temperature field one should first obtain the solution of the equations at the fundamental frequency:

$$\left(\frac{\partial^2}{\partial z^2} - p^2 \right) \tilde{T}_\omega = 0; \quad \frac{\partial}{\partial z} \tilde{T}_\omega = -\frac{J_\omega}{k_0} \quad \text{at } z=0 \quad (8)$$

$$k_0 \frac{\partial}{\partial z} \tilde{T}_\omega \Big|_{h_i+0} = 0; \quad \tilde{T}_\omega \Big|_{h_i+0} = 0 \quad (9)$$

with $p \equiv p(\omega)$ and $J_\omega \equiv (1 - R_0)I_\omega$. Next the 2ω temperature field may be found from

$$\left(\frac{\partial^2}{\partial z^2} - 2p^2 \right) \tilde{T}_{2\omega} = -\frac{1}{4} \left[\delta_2 \frac{\partial^2}{\partial z^2} - \delta_1 (2p^2) \right] \tilde{T}_\omega^2 \\ \frac{\partial}{\partial z} \tilde{T}_{2\omega} = -\frac{1}{4} \delta_2 \frac{\partial}{\partial z} \tilde{T}_\omega^2 - \frac{1}{2} \delta_3 \left(\frac{J_\omega}{k_0} \right) \tilde{T}_\omega \quad \text{at } z=0 \quad (10)$$

$$k_0 \left(\frac{\partial}{\partial z} \tilde{T}_{2\omega} + \frac{\delta_2}{4} \frac{\partial}{\partial z} \tilde{T}_\omega^2 \right. \\ \left. + \frac{1}{4} \frac{\partial^2}{\partial z^2} \tilde{T}_\omega \sum_{j=1}^i \beta_j^* \int_{h_{(j-1)0}}^{h_{j0}} \tilde{T}_\omega dz \right) \Big|_{h_i+0} = 0 \quad (11)$$

$$\left(\tilde{T}_{2\omega} + \frac{1}{4} \frac{\partial}{\partial z} \tilde{T}_\omega \sum_{j=1}^i \beta_j^* \int_{h_{(j-1)0}}^{h_{j0}} \tilde{T}_\omega dz \right) \Big|_{h_i+0} = 0 \quad (12)$$

Eqs. (8)–(12) provide the general mathematical formalism for the examination of the thermal-wave second-harmonic field in layered structures in 1-D geometry. Owing to the fact that Eqs. (8)–(12) are linear, their general analytical solution is available and can be obtained for specific structures, when necessary. In the present work we will present the detailed analysis of the three simplest situations: a free-standing film in a vacuum; a homogeneous film with the back surface in contact with a heat sink; and a bilayered structure composed of two films with the same linear but different non-linear thermophysical parameters. This investigation will reveal the most important peculiarities of the 2ω generation in thin films, and at the same time will provide a means for qualitative predictions of the second-harmonic temperature-field behavior in more complicated structures.

2.1. Free-standing film

In the case of a thin solid film in a gaseous ambient, the thermal flux through the back surface of the film may be neglected. The boundary conditions (9), (11) and (12) then reduce to

$$\frac{\partial}{\partial z} \tilde{T}_\omega = 0 \quad \frac{\partial}{\partial z} \tilde{T}_{2\omega} = -\frac{\beta^*}{4} \frac{\partial^2}{\partial z^2} \tilde{T}_\omega \int_0^h \tilde{T}_\omega dz$$

at $z = h$ (13)

where h is the film thickness. The exact solution of the problem described by Eqs. (8), (10), (13) may be presented in the form:

$$\begin{aligned} \tilde{T}_\omega &= \left(\frac{J_\omega}{k_0 p \sinh(ph)} \right) \cosh[p(z-h)] & (14) \\ \tilde{T}_{2\omega} &= -\frac{1}{8} \left(\frac{J_\omega}{k_0 p \sinh(ph)} \right)^2 \frac{1}{\sinh(\sqrt{2} ph)} \\ &\times (\sqrt{2} \beta^* \sinh(ph) \cosh(\sqrt{2} pz) \\ &+ \{\delta_1 + (2\delta_2 - \delta_1) \cosh[2p(z-h)]\} \sinh(\sqrt{2} ph) \\ &+ \sqrt{2} (\delta_1 - \delta_2 - \delta_3) \sinh(2ph) \cosh[\sqrt{2} p(z-h)]) \end{aligned}$$

(15)

According to Eq. (15), at the back interface ($z = h$) of the thermally thick film ($|p|h \gg 1$) the dominant contribution to the second harmonic is caused by the film "breathing" mode:

$$\begin{aligned} \tilde{T}_{2\omega}|_{z=h \gg 1/|p|} &\approx -\frac{1}{2\sqrt{2}} \left(\frac{J_\omega^2}{C_0 k_0 \omega} \right) e^{-ph} \\ &\times [\beta^* + 2(\delta_1 - \delta_2 - \delta_3) e^{-(\sqrt{2}-1)ph}] \\ &\approx -\frac{i}{2\sqrt{2}} \left(\frac{J_\omega^2}{C_0 k_0 \omega} \right) \beta^* e^{-ph} \end{aligned}$$

Nevertheless, this limiting case is not important in practice, as the signal is too small owing to the small parameter $|\exp(-ph)| \ll 1$. The analysis of the solution, Eq. (15), showed that in nearly all practically interesting situations one can neglect the contribution from the thermal expansion as a consequence of the inequalities $|\beta^*| \ll |\delta_1|, |\delta_2|$, which is usually the case with solids [7,8].

In the important case where the system under consideration includes gas-filled layers (e.g. adhesive layers or contacts at rough surfaces, which may also be gas-containing layers), both the effective thermal conductivity and the corresponding non-linear parameter δ_2 can be reduced significantly. Under these conditions, the "breathing" of the layer may be the main (and

extremely effective) cause of nonlinearity, acting in a manner similar to gas-filled cracks [9].

In our search for ways to enhance spatial resolution of non-linear photothermal depth-profiling, let us examine the asymptotic behavior of the solutions, Eqs. (14) and (15), for thermally thin films. In the limit $|p|h \ll 1$ the expressions of Eqs. (14) and (15) simplify:

$$\begin{aligned} \tilde{T}_\omega|_{|p|h \ll 1} &\approx i \left(\frac{J_\omega}{C_0 \omega h} \right) \{1 + i[(z-h)^2 - h^2/3]q^2\} \\ &\approx i \left(\frac{J_\omega}{C_0 \omega h} \right) \end{aligned}$$

(16)

$$\begin{aligned} \tilde{T}_{2\omega}|_{|p|h \ll 1} &\approx \frac{1}{4} \left(\frac{J_\omega}{C_0 \omega h} \right)^2 \left[\delta_1 - \delta_3 + \frac{\beta^*}{2} \right. \\ &- i \left\{ 2\delta_2[(z-h)^2 - h^2/3] - 2\delta_3(z-h)^2 \right. \\ &\left. \left. + \beta^* \left(z^2 - \frac{h^2}{2} \right) \right\} q^2 \right] \end{aligned}$$

(17)

where we have introduced the real part of the thermal wavenumber $q = \text{Re}(p) = [\omega/(2D_0)]^{1/2}$. This is the inverse of the thermal diffusion length $\mu_q = q^{-1}$. The solution, Eq. (16), shows that the temperature field at the fundamental frequency is spatially quasi-homogeneous in the thermally thin film (i.e. with in-phase variations of T_ω throughout the thickness of the film). The spatial distribution of the second-harmonic temperature field, Eq. (17), is generally more complicated: according to Eq. (17) there are two phase-shifted contributions to the 2ω temperature field which depend on different combinations of the non-linear parameters $\delta_1, \delta_2, \delta_3$ and β^* . The relative magnitude of these two contributions is controlled not only by the dimensionless parameter $(qh)^2 \ll 1$, but also depends on the spatial coordinate and the relative magnitudes of the various non-linearities. Therefore, the second term in the curly brackets of Eq. (17) generally cannot be omitted, as was done in Eq. (16). Note that the non-linearity associated with the dependence of the thermal conductivity on temperature does not contribute to the first term in Eq. (17), in agreement with the fact that this non-linearity operates only in spatially inhomogeneous temperature fields T_ω . The contribution of this kind of non-linearity in Eq. (17) is principally spatially inhomogeneous. For example, it is evident that the component of the second-harmonic thermal-wave field which is proportional to δ_2 exhibits a π phase shift in Eq. (17) when proceeding from the front to the back surface of the film.

The 2ω temperature at the back surface ($z = h$) of the irradiated film is given by

$$\tilde{T}_{2\omega}|_{z=h \ll 1/\rho} \approx \frac{1}{4} \left(\frac{J_\omega}{C_0 \omega h} \right)^2 \times \left[\delta_1 - \delta_3 + \frac{\beta^*}{2} + i \left(\frac{2}{3} \delta_2 - \frac{\beta^*}{2} \right) (qh)^2 \right] \quad (18)$$

Let us introduce compact notations for the important combinations of non-linear parameters

$$\Delta_1 \equiv \delta_1 - \delta_3 + \frac{\beta^*}{2} \quad \Delta_2 \equiv \frac{2\delta_2}{3} - \frac{\beta^*}{2}$$

According to Eq. (18) one can neglect the imaginary component on the right-hand side even in thermally thin films ($qh \ll 1$), if and only if the inequality $|\Delta_1| \geq |\Delta_2|$ also holds. If $|\Delta_1/\Delta_2| \ll 1$, then both combinations of non-linearities play an important role in the non-linear thermal-wave signal generation in thermally thin films. With the use of Eq. (18) the phase of the second-harmonic thermal wave may be described as follows

$$\phi_{2\omega} = -\pi \operatorname{sgn} \Delta_1 - \tan^{-1} \left[\frac{\Delta_2}{\Delta_1} (qh)^2 \right] \quad (19)$$

Consequently, the 2ω phase depends weakly on modulation frequency (i.e. on $(qh)^2$) if $|\Delta_2/\Delta_1| \ll 1$. However, if $|\Delta_2/\Delta_1| \gg 1$ then the $\phi_{2\omega}$ exhibits significant shift ($-(\pi/2) \operatorname{sgn}(\Delta_2/\Delta_1)$) with the increase of frequency across the regimes $(qh)^2 \ll |\Delta_1/\Delta_2| \ll 1$ to $|\Delta_1/\Delta_2| \ll (qh)^2 \ll 1$. One can expect the steepest phase variations for

$$\mu_q \approx |\Delta_2/\Delta_1|^{1/2} h \gg h \quad (20)$$

It is well known that, using fundamental frequency detection (i.e. with linear photothermal techniques) to measure the film thickness h , one should have laser-beam intensity modulation at frequencies $\omega_L \sim 2D_0/h^2$, which provide thermal-wave penetration length $\mu_q \sim h$. This statement follows from the solution Eq. (14). According to Eq. (20), using the detection of the thermal wave second harmonic (i.e. with non-linear photothermal techniques) it is possible to measure the thickness of thin films with $|\Delta_2/\Delta_1| \gg 1$ at significantly lower frequencies

$$\omega_{NL} \sim |\Delta_1/\Delta_2| \omega_L \ll \omega_L \quad (21)$$

This implies that the thicknesses of thermally thin films may be measured non-linearly, Eq. (20).

This non-linear effect originates in the competition of different mechanisms giving rise to thermal-wave

second-harmonic generation. Not only is it important that the efficiencies of different mechanisms demonstrate different dependencies on modulation frequency, but also that their contributions to the total 2ω temperature field should be significantly phase-shifted.

Note that the β^* contribution to Δ_2 can be omitted for most solids, as a consequence of $|\beta^*| \ll |\delta_2|$. The thermal expansion contribution (β^*) to Δ_1 can be neglected in comparison with $|\delta_1|$ only if the non-linearity associated with $C(T)$ is not compensated in Δ_1 by the component associated with the reflectivity $R(T)$. However, it should be mentioned that, since

$$\delta_1 = \frac{1}{C} \frac{\partial C}{\partial T} = \frac{1}{\rho} \frac{\partial \rho}{\partial T} + \frac{1}{C_p} \frac{\partial C_p}{\partial T}$$

and

$$\frac{1}{\rho} \frac{\partial \rho}{\partial T} \sim -\beta^*$$

then in the same approximation the contribution from the mass-density dependence on temperature may be neglected. Furthermore, it would be immaterial under these conditions to discriminate between specific heats at constant pressure C_p and constant volume C_v [10].

To illustrate the predicted 2ω phase behavior, we have presented in Fig. 1 the dependence of $\phi_{2\omega}(z = h)$ on (qh) for various values of the dimensionless parameter $B \equiv (\delta_1 - \delta_3)/\delta_2$. We have considered for

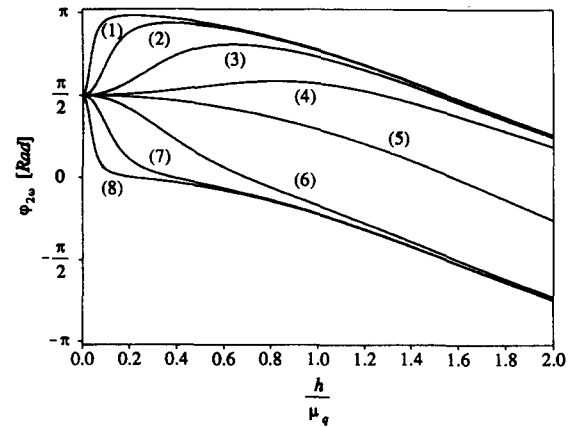


Fig. 1. Dependence of the thermal-wave second-harmonic phase at the back surface of a free-standing film on the relative magnitude of the film thickness h and fundamental-frequency thermal-wave penetration length μ_q . The plots are valid for $\delta_1 - \delta_3 > 0$ and for several values of the dimensionless parameter $B \equiv (\delta_1 - \delta_3)/\delta_2$ equal to: -10^{-3} (curve 1); -10^{-2} (curve 2); -10^{-1} (curve 3); -1 (curve 4); 1 (curve 5); 10^{-1} (curve 6); 10^{-2} (curve 7); and 10^{-3} (curve 8). Here $\delta_1 = (1/C)(\partial C/\partial T)$, $\delta_2 = (1/k)(\partial k/\partial T)$ and $\delta_3 = (1-R)(\partial R/\partial T)$.

simplicity $\beta^* \rightarrow 0$, which implies $B \approx (2/3)|\Delta_1/\Delta_2|$. The plots have been calculated with the help of the general solution, Eq. (15), and are presented only for the special case $\delta_1 - \delta_3 = \Delta_1 > 0$. In the case $\delta_1 - \delta_3 < 0$ an additional phase shift equal to $(-\pi)$ should be introduced. Fig. 1 demonstrates the transition from the thermally thin regime to the thermally thick regime in the thin film. Steep phase variations for $|\Delta_1/\Delta_2| \approx (\delta_1 - \delta_3)/\delta_2 \ll 1$ in the thermally thin films are clearly observable.

2.2. Film contacting a heat sink

In the case of a thin film with spatially stabilized back surface temperature, the boundary conditions Eqs. (9), (11) and (12) reduce to:

$$\tilde{T}_\omega = 0 \quad \tilde{T}_{2\omega} = -\frac{\beta^*}{4} \frac{\partial}{\partial z} \tilde{T}_\omega \int_0^h \tilde{T}_\omega dz;$$

at $z = h$ (22)

The exact solution of the problem described by Eqs. (8), (10) and (22) may be expressed in the form:

$$\tilde{T}_\omega = -\left[\frac{J_\omega}{k_0 p \cosh(ph)} \right] \sinh[p(z-h)] \quad (23)$$

$$\begin{aligned} \tilde{T}_{2\omega} = & -\frac{1}{8} \left[\frac{J_\omega}{k_0 \cosh(ph)} \right]^2 \frac{1}{\cosh(\sqrt{2} ph)} \\ & \times (2 \left\{ \delta_1 - \delta_2 + \beta^*[1 - \cosh(ph)] \right. \\ & \times \cosh(\sqrt{2} pz) + \{ \delta_1 + (\delta_1 - 2\delta_2) \\ & \times \cosh[2p(z-h)] \} \cosh(\sqrt{2} ph) \\ & \left. - \sqrt{2} (\delta_1 - \delta_2 - \delta_3) \sinh(2ph) \sinh[\sqrt{2} p(z-h)] \right\}) \end{aligned} \quad (24)$$

In the thermally thin film approximation ($|p|h \ll 1$) the solutions Eqs. (23) and (24) become

$$\begin{aligned} \tilde{T}_\omega & \approx -\left(\frac{J_\omega}{k_0} \right) (z-h) \{ 1 + i[h^2 - (z-h)^2]/3q^2 \} \\ & \approx -\left(\frac{J_\omega}{k_0} \right) (z-h) \end{aligned} \quad (25)$$

$$\begin{aligned} \tilde{T}_{2\omega} & \approx -\frac{1}{4} \left(\frac{J_\omega}{k_0} \right)^2 h^2 \left[\delta_2 - 2\delta_3 - \frac{\beta^*}{2} \right. \\ & \left. - i \left(\delta_1 - \frac{7}{3} \delta_2 + \frac{16}{3} \delta_3 + \frac{11}{6} \beta^* \right) (qh)^2 \right] \end{aligned} \quad (26)$$

Note that Eq. (26) is already compactly written for $z=0$, i.e. at the front surface of the film.

An analysis similar to the one presented in Section 2.1 demonstrates the enhanced sensitivity of the 2ω phase to variations of the modulation frequency, again, under the condition $|\Delta_1/\Delta_2| \ll 1$. This time, however, Δ_1 and Δ_2 are governed by different combinations of the familiar non-linear parameters δ_1 , δ_2 , δ_3 and β^* :

$$\begin{aligned} \Delta_1 & = \delta_2 - 2\delta_3 - \beta^*/2 \\ \Delta_2 & = \delta_1 - \frac{7}{3} \delta_2 + \frac{16}{3} \delta_3 + \frac{11}{6} \beta^* \end{aligned} \quad (27)$$

In the previous case of a free-standing film (Section 2.1), the thermal-conductivity dependence on temperature was shown to contribute only to the term Δ_2 , owing to the particular set of non-linear parameters assigned to the definition of this term. As a result, the domination of the non-linearity associated with $k(T)$ is sufficient condition to achieve $|\Delta_1/\Delta_2| \ll 1$. In the case of a film in contact with a heat sink, it is the non-linearity associated with $C(T)$ that contributes to Δ_2 and *does not* contribute to Δ_1 . In the system under consideration, the efficiency of the second-harmonic generation mechanism associated with $C(T)$ decreases with decreasing modulation frequency. This is caused by the fact that according to Eq. (1) this kind of non-linearity is related to temporal variations of temperature, while the boundary conditions determine the magnitude (spatial distribution and amplitude) of the temperature T_ω at low frequencies, Eq. (25). As a result, this non-linearity makes a contribution to the 2ω temperature field at the surface proportional to $\delta_1 \omega \sim \delta_1 q^2$. The main contributions from the rest of the non-linearities become frequency-independent in a thermally thin film ($qh \ll 1$) owing to the nature of the T_ω field.

Therefore, the domination of the non-linearity associated with $C(T)$ suffices to achieve $|\Delta_1/\Delta_2| \ll 1$ in the regime described by Eqs. (26) and (27). Note that $|\delta_2/\delta_1| \sim 0.1$ in certain polymers (for example, Plexiglas) at room temperature. Nevertheless, this is not a necessary condition. One can also try to minimize $|\Delta_1/\Delta_2|$ by choosing appropriate initial temperature T_0 or the irradiation wavelength. In any case, and in agreement with Eqs. (20) and (21), an enhanced spatial resolution of non-linear photothermal depth profilometry is expected for $|\Delta_1/\Delta_2| \ll 1$.

The possibility of minimizing $|\Delta_1/\Delta_2|$ arises in general from the fact that $k = k(T)$ is a non-monotonic function of temperature. Usually $k(T)$ increases at low temperatures immediately above $T=0$ K, as a consequence of the increase in the population of particles (or quasi-particles) participating in the energy transport: this amounts to an increase in the heat capacity. At sufficiently high temperatures, however,

conventionally $k(T)$ decreases with increasing temperature of the solid, a result of the domination of thermal transport by scattering processes. Therefore, by varying the initial temperature one can change not only the absolute value, but also the sign of the non-linear parameter δ_2 in order to minimize $|\Delta_1/\Delta_2|$. Near the extremum (maximum) of the $k = k(T)$ curve, i.e. in the region $\delta_2 \approx 0$, the thermal "breathing" of the surface film, which is directly associated with the parameter β^* , may become important even for solid films.

2.3. A pair of thin films

Let us examine the bilayered structure consisting of two films $0 \leq z \leq h$ and $h \leq z \leq h + H$ in a gaseous ambient. We will consider the linear thermoelastic parameters of both films to be the same. This is a sufficient condition for the absence of thermal-wave reflections at the interface $z = h$. Then a description of the temperature field at the fundamental frequency may be obtained by substituting $h \rightarrow h + H$ in Eq. (14). The boundary conditions Eqs. (11) and (12) further reduce to:

$$\left(\frac{\partial}{\partial z} \tilde{T}_{2\omega} + \frac{\delta_2}{4} \frac{\partial}{\partial z} \tilde{T}_{2\omega} \right) \Big|_{z=h-0}^{h+0} = 0, \quad \tilde{T}_{2\omega} \Big|_{z=h-0}^{h+0} = 0$$

$$\frac{\partial}{\partial z} \tilde{T}_{2\omega} + \frac{1}{4} \frac{\partial^2}{\partial z^2} \tilde{T}_{2\omega} \left(\beta_h^* \int_0^h \tilde{T}_{2\omega} dz + \beta_H^* \int_h^{h+H} \tilde{T}_{2\omega} dz \right) = 0 \quad \text{at } z = h + H \quad (28)$$

In what follows, we introduce the superscripts (h) and (H) to denote the non-linear thermoelastic parameters of different layers. The solution of the problem described by Eqs. (10) and (28) at the front surface, $z = 0$, may be written as follows:

$$\tilde{T}_{2\omega} \Big|_{z=0} = -\frac{1}{8} \left\{ \frac{J_\omega}{k_0 p \sinh[p(H+h)]} \right\}^2$$

$$\times \frac{1}{\sinh[\sqrt{2} p(H+h)]}$$

$$\{ -\sqrt{2} \delta_3 \sinh[2p(H+h)] \cosh[\sqrt{2} p(H+h)]$$

$$+ \Phi(\beta_h^*, \delta_1^h, \delta_2^h, H+h)$$

$$- \Phi(\Delta\beta^*, \Delta\delta_1, \Delta\delta_2, H) \} \quad (29)$$

where we have introduced the function

$$\Phi(\beta^*, \delta_1, \delta_2, \eta) \equiv \sqrt{2} \beta^* \sinh(p\eta)$$

$$+ [\delta_1 + (2\delta_2 - \delta_1) \cosh(2p\eta)]$$

$$\times \sinh(\sqrt{2} p\eta) - \sqrt{2} (\delta_2 - \delta_1)$$

$$\times \sinh(2p\eta) \cosh(\sqrt{2} p\eta)$$

with the notations

$$\Delta\delta_1 = \delta_1^h - \delta_1^H \quad \Delta\delta_2 = \delta_2^h - \delta_2^H \quad \Delta\beta^* = \beta_h^* - \beta_H^*$$

for the differences in non-linear parameters of the layers. According to Eq. (29), only the last term in the curly brackets describes the influence of the 1non-linear thermal inhomogeneity on the 2ω signal. In the limit $H \rightarrow 0$, Eq. (29) yields Eq. (15), as expected. We have examined the solution Eq. (29) in two limiting cases of thermally thick ($|p|H \gg 1$) and thermally thin ($|p|H \ll 1$) backing.

For the description of a coating on a semi-infinite substrate (i.e. $H \rightarrow \infty$), we have obtained from Eq. (29)

$$\tilde{T}_{2\omega} = -\frac{1}{4} \left(\frac{J_\omega^2}{C_0 k_0 \omega} \right) (\sqrt{2} - 1)$$

$$\{ [(\delta_1^h - 2\delta_3) + \sqrt{2} (\delta_2^h - \delta_3)]$$

$$- (\Delta\delta_1 + \sqrt{2} \Delta\delta_2) \exp[-(2 + \sqrt{2})ph] \} \quad (30)$$

It is worth noting the complete absence of the influence of the thermal expansion on the 2ω temperature in this regime. In the most interesting situation of a thermally thin coating ($|p|h \ll 1$), the solution Eq. (30) transforms to

$$\tilde{T}_{2\omega} \Big|_{z=0} \approx -\frac{i}{4} \left(\frac{J_\omega^2}{k_0 \omega} C_0 \right)$$

$$(\sqrt{2} - 1) \{ (\delta_1^H - 2\delta_3) + \sqrt{2} (\delta_2^H - 2\delta_3) \}$$

$$+ (1 - i) (\Delta\delta_1 + \sqrt{2} \Delta\delta_2) (qh) \} \quad (31)$$

Eq. (31) exhibits significant 2ω phase variations, which may occur even for thermally thin coatings under the condition

$$\Delta_3 \equiv |(\delta_1^H - 2\delta_3) + \sqrt{2} (\delta_2^H - \delta_3)| \ll |\Delta_4|$$

$$\equiv |\Delta\delta_1 + \sqrt{2} \Delta\delta_2| \quad (32)$$

If the inequality (32) holds, then a phase shift on the order of $\pm \pi/4$ will occur when

$$\mu_q \approx |\Delta_4/\Delta_3| h \gg h \quad \text{or} \quad \omega_{NL} \sim |\Delta_3/\Delta_4|^2 \omega_L \ll \omega_L$$

Given that the non-linear parameters δ_1 and δ_2 of the coating contribute only to Δ_4 , we can say that a sufficient condition to satisfy the inequality (32) is the domination of the signal by the non-linearities associated with the dependences $C(T)$ and $k(T)$ of the film. Another possibility to satisfy condition (32) is to compensate the thermal non-linearities associated with the dependences $C(T)$ and $k(T)$ of the backing by the non-linearity associated with the $R(T)$ of the coating. This observation is consistent with the fact that in the case of a semi-infinite sample [5], the 2ω temperature

is zero at the irradiated surface $z=0$ when $(\delta_1 - 2\delta_3) + \sqrt{2}(\delta_2 - \delta_3) = 0$.

However, in the system considered here the physical situation is more interesting, as the parameters of different materials may participate in the compensation of non-linear effects at low frequencies. We should also mention that the first correction to the low-frequency limit increases with frequency rise relatively more steeply in a coating than in a free-standing film. Actually, the second term in the curly brackets of Eq. (31) is proportional to $(qh) \sim \sqrt{\omega}$ in a coating, while the same second term in Eqs. (17) and (18) is proportional only to $(qh)^2 \sim \omega$ in a free-standing film. For $(qh) \ll 1$ the former dependence is stronger. From Eq. (31) it can be seen that the signal contributions from the nonlinearities associated with $C(T)$ and $k(T)$ of the coating are directly proportional to the thickness of the coating.

For the thermally-thin bilayered system, assuming $|p|H \ll 1$, we have obtained from Eq. (29)

$$\begin{aligned} \tilde{T}_{2\omega}|_{z=0} \approx & \frac{1}{4} \left(\frac{J_\omega}{C_0 \omega} \right)^2 \frac{1}{(H+h)^3} \\ & \times \left\{ \left(\delta_1^h - \delta_3 + \frac{\beta_h^*}{2} \right) h \right. \\ & + \left(\delta_1^H + \delta_3 + \frac{\beta_H^*}{2} \right) H \\ & - i \left[\left(\frac{4}{3} \delta_2^h - 2\delta_3 - \frac{\beta_h^*}{2} \right) (H+h)^3 \right. \\ & \left. - \left(\frac{4}{3} \Delta \delta_2 - \frac{\Delta \beta^*}{2} \right) H^3 \right. \\ & \left. + \frac{2}{3} (2\Delta \delta_1 + \Delta \beta^*) (2H+h) H h \right] q^2 \left. \right\} \quad (33) \end{aligned}$$

From earlier considerations (Sections 2.1 and 2.2) we can state that non-linear photothermal depth profiling of thermally thin layers should be possible, provided that real and imaginary parts of the expression in the curly brackets of Eq. (33) are of the same order of magnitude, even for $q(H+h) \ll 1$. Under this condition, and in the experimentally interesting situation $h \ll H$, we can rewrite the curly brackets in Eq. (33) to obtain

$$\tilde{T}_{2\omega} \approx \Delta_1^h + \Delta_1^H H - i(3\Delta_2^h h + \Delta_2^H H)(qH)^2 \quad (34)$$

with $\Delta_1 \equiv \delta_1 - \delta_3 + \beta^*/2$ and $\Delta_2 \equiv (4\delta_2/3) - 2\delta_3 - \beta^*/2$. Note that the inequality has already been taken into account in Eq. (34). Therefore, from Eq. (34) one can

expect significant changes in the 2ω phase when

$$qH \sim \left| \frac{\Delta_1^h h + \Delta_1^H H}{3\Delta_2^h h + \Delta_2^H H} \right|^{1/2} \ll 1 \quad (35)$$

In a manner similar to the case of a free-standing film (Section 2.1), in order to realize this phase regime it is sufficient to have a system with the dominant non-linear role associated with $k(T)$, since δ_2^h and δ_2^H contribute only to Δ_2 . This analogy becomes even more evident if one notices that the parameters Δ_1 introduced in Eqs. (35) and (19) are identical. Thus, the solution Eqs. (34) and (35) demonstrates how the relative contributions of different layers to the total signal are weighted.

It is more difficult to extract information on the coating thickness h when the backing is also thermally thin than the case of a thermally-thick backing. Actually, according to Eq. (35), if one of the layers is "more linear" than the other (i.e. $|\Delta_{1,2}^h| h \ll |\Delta_{1,2}^H| H$ or vice versa), the information on h is lost:

$$qH \sim |\Delta_1^H / \Delta_2^H|^{1/2}$$

or

$$qH \sim |\Delta_1^h / 3\Delta_2^h|^{1/2}$$

In mixed situations, that is, for $|\Delta_1^h| h \ll |\Delta_1^H| H$ $|\Delta_2^h| h \gg |\Delta_2^H| H$ or vice versa, the information on h appears together with that on backing thickness H :

$$q(Hh)^{1/2} \sim |\Delta_1^H / 3\Delta_2^h|^{1/2}$$

or

$$qH^{3/2} h^{-1/2} \sim |\Delta_1^h / \Delta_2^H|^{1/2}$$

3. Conclusions

The present theoretical analysis of thermal-wave second-harmonic generation in thin films and coatings demonstrates the possibility of non-linear photothermal depth profilometry of thermally-thin layers. It was shown that thicknesses much smaller than the thermal-wave penetration (diffusion) length may be measured from the second-harmonic thermal-wave phase variations. This can be achieved in a free-standing film in which the dominant non-linearity is related to the dependence on temperature of the thermal conductivity; or in films which are in contact with a heat bath, and in which the dominant non-linearity is associated with the dependence on temperature of the heat capacity. The thickness of a thermally-thin coating on a semi-infinite substrate can

also be measured using a non-linear photothermal technique if the non-linearities of the substrate are compensated by the non-linearity associated with the dependence on temperature of the optical reflectivity of the coating; or in the case where the dominant non-linearities are related to the $C(T)$ and $k(T)$ dependences of the coating. In summary, the one-dimensional theory presented in this work predicts the dependence of the depth resolution of non-linear photothermal microscopy on specific combinations of important non-linear parameters of thin solid films.

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