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THERMAL PROPERTIES OF THIN FILMS STUDIED BY ULTRAFAST LASER SPECTROSCOPY: THEORY AND EXPERIMENT

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The one-dimensional non-homogeneous hyperbolic energy equation within a semi-infinite domain, applied to pump-probe transient reflectance measurements for subpicosecond and picosecond laser pulses was studied. The result of this study is an analytical model in the form of a Volterra-type integral equation that describes the surface temperature response of the thin film induced by an ultra-short laser pulse and takes into account contributions of the transient heat flux and the volumetric heat source. The criterion based on dimensionless time $\xi_p = t/2\tau$ (where τ is the relaxation time of phonons due to collisions) is introduced, in order to predict the temperature response caused by the surface heat flux and/or volumetric source. This analytical solution is validated by using experimental pump-probe transient reflectance measurements of thin gold with a time resolution of 50 fs. A good agreement between the experimental results and the theoretical model is found.

1. Introduction

Knowledge of heat transfer processes in thin films, caused by ultrafast laser pulses, is important for their practical applications in microelectronics [1], data storage and micro-electro mechanical devices [2, 3], etc.

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Attaining analytical solutions for transient heat problems in a certain domain is complex due to the mathematical intricacies involved in solving the differential equation describing the phenomenon (see, for instance, [4, 5, 6]). In general, numerical simulations are the only choice for solving the equation.

When investigating a relationship between heat flux and temperature at a particular location, for example at the boundary (surface) of the domain, the heat conduction equation should first be solved within the whole domain.

There are practical situations in thermal engineering where a relationship between heat flux and surface (local) temperature would suffice. For example, the ultrafast pump-probe transient reflection method (TRM) was used to measure the thermal conductivity of various materials including thin films [7, 8, 9]. The TRM consists of heating the material surface with a ultrashort laser beam and then tracking the decay of the surface temperature with time (by determining the surface reflectivity). Thus, the time-dependent evolutions of the surface temperature proportional to the surface reflectivity [5, page 119] and the heat flux are known.

Thermal properties of a material can then be extracted by fitting the experimental data (i.e., the decay of the surface temperature with time) to the analytical solution attained by solving the transient heat transfer equation that describes the laser-heating process. This method has three main limitations as below: first, in order to obtain an analytical solution for the surface temperature, one needs to get a solution of the diffusion equation for both the surface and the entire domain; second, one needs to know the specific heat and the density of the material in order to obtain analytical transient solutions; third, an analytical solution for the TRM exists under assumption that laser radiation is absorbed at the surface of the film for opaque materials. For semitransparent materials, only numerical solutions can be attained.

To eliminate these limitations, the relatively simple methodology for deriving a single, general, fractional equation relating to volumetric heating, surface heat flux, surface temperature, and thermal properties was presented in [10]. This approach, based on fractional calculus, was presented by Lage and Kulish [11] to be very effective when applied to solving transient diffusion problems and was further generalized by Frankel for finite domains [12].

It is known that the classical assumptions of heat transfer become no longer valid for heat transfer processes induced by laser with picosecond and subpicosecond pulses. Indeed, it becomes necessary to account for the time lag (relaxation time) between the temperature gradient and the heat flux induced by it that is postulated by Cattaneo [13] and Vernotte [14], independently. In

particular, this fact leads to the hyperbolic heat conduction equation that indicates that energy is transmitted by means of thermal waves and dissipated due to diffusion [15]. Based on this methodology, the authors of Ref. [16] have established the relationship between the local temperature and its spatial derivative within a one-dimensional semi-infinite domain taking into account the finite speed of thermal wave propagation. Furthermore, in Ref. [16] the volumetric source was neglected because the penetration depth in metals is of the order of a few nanometers.

Although the penetration depth is a very small value, it will be shown that the volumetric source is a basic term that defines the surface temperature response in comparison with the contribution of a surface heat flux under the irradiation by a subpicosecond laser pulse. Thus, the volumetric source cannot be neglected in a practical model.

This paper focuses on the study of the one-dimensional non-homogeneous hyperbolic energy equation, applied to TRM, restricting its analysis to the heat transfer problem in a semi-infinite domain. The obtained Volterra-type integral equation takes into account also the volumetric heat source, which usually is neglected. This analytical solution is validated by using experimental pump-probe transient reflectance measurements of a thin gold film with a time resolution of 50 fs.

2. Mathematical model

Theoretical and numerical investigation of laser interaction with metallic films by use of the two-temperature model (TTM) was proposed by Anisimov [17, 18]. TTM is presented in the form of two coupled nonlinear parabolic partial differential equations that describe the interaction of the electron and phonon (lattice) gasses.

However, the analysis of experimental results shows that the thermalization of the electron gas due to electron-electron interactions occurs within few hundred femtoseconds [19, 20]. This time is relatively small compared with the response time of surface temperature (> 10 ps). Therefore, in this study, the heating of the electron gas is assumed to be instantaneous. It means that the equilibrium between electron and phonon gases happens after the laser excitation. Then Cattaneo's law is applied to the heat flux in the phonon subsystem [21, 22]. A more detailed mathematical description of this stage is shown in [23].

Hence, the TTM is reduced to a one-dimensional hyperbolic heat equation with a time-dependent volumetric heat source [24], which is

$$\tau \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} + \frac{1}{C} \left[S(x, t) + \tau \frac{\partial}{\partial t} S(x, t) \right] \quad (1)$$

where $T = T(x, t)$ is the scalar temperature field, t is the time, x is the spatial variable along the direction of the laser beam propagation, $S(x, t)$ is the time-dependent volumetric heat source and τ is the relaxation time in phonon collision, which is defined as

$$\tau = \alpha / c^2 \quad (2)$$

where c is the speed of sound [15]. Due to the assumption that the electron gas heats instantaneously, the electron-phonon subsystems are at equilibrium. Thus, the parameters of Eqn. (1), namely, the thermal diffusivity α , and the volumetric heat capacity C can be defined as for the bulk material.

For the further analysis, Eqn. (1) is rewritten in a dimensionless form which is

$$\frac{\partial^2 \theta}{\partial \xi^2} + 2 \frac{\partial \theta}{\partial \xi} = \frac{\partial^2 \theta}{\partial \eta^2} + \left[\tilde{q} + \frac{1}{2} \frac{\partial \tilde{q}}{\partial \xi} \right] \quad (3)$$

where $\xi = t/(2\tau)$, $\eta = x/(2\alpha\tau)$, θ and $\tilde{q}$ are the dimensionless temperature and volumetric source, respectively.

The details of this model including the boundary and initial conditions have been described in the previous study (see Appendix of Ref. [25]). For the surface temperature ($\eta = 0$), it becomes

$$\begin{aligned} \theta(\xi) = & \int_0^\xi \left[\tilde{q}^{//}(\xi^*) + \frac{1}{2} \frac{\partial \tilde{q}^{//}(\xi^*)}{\partial \xi^*} \right] I_0(\xi - \xi^*) e^{-(\xi - \xi^*)} d\xi^* \\ & + \frac{\Delta \eta^2}{4\sqrt{1 + \Delta \eta^2}} \sqrt{\frac{\pi}{a}} \int_0^\xi \left\{ \left(1 + \frac{1}{2} s_1\right) e^{\frac{B_1^2}{A}} \left[\operatorname{erf}(\sqrt{A}\xi^* + \frac{B_1}{\sqrt{A}}) \right. \right. \\ & \left. \left. - \operatorname{erf}(\frac{B_1}{\sqrt{A}}) \right] - \left(1 + \frac{1}{2} s_2\right) e^{\frac{B_2^2}{A}} \left[\operatorname{erf}(\sqrt{A}\xi^* + \frac{B_2}{\sqrt{A}}) \right. \right. \\ & \left. \left. - \operatorname{erf}(\frac{B_2}{\sqrt{A}}) \right] \right\} (\delta(\xi - \xi^*) - \frac{1}{\Delta \eta} I_0(\xi - \xi^*) e^{-(\xi - \xi^*)}) d\xi^*, \end{aligned} \quad (4)$$

where $I_0(\xi)$

is the modified Bessel function, $\delta(\xi)$ is the Dirac delta function, $\text{erf}(\xi)$ is the Gauss error function [26],

$$s_{1,2} = -1 \pm \frac{1}{\Delta\eta} \sqrt{1 + \Delta\eta^2}, B_{1,2} = s_{1,2} - 2 \frac{a}{\xi_p^2} \xi_b \quad \text{and} \quad A = \frac{a}{\xi_p^2}$$

Thus, obtained model (4) describes the surface temperature response of the thin film caused by an ultrashort laser pulse and considers contributions of the transient heat flux (given by the first integral in (4)) and the volumetric heat source (the second integral in (4)). Note also, that Eqn. (4) can be used to determine the penetration depth, κ , in the case when the temperature response is measured and the incitation heat flux is known.

Figure 1: Pump-probe setup: WLC (White Light Continuum); OPO (Optical Parametric Oscillator); GTP (Glan-Thompson Polarizer).

3. Model Validation and Analysis

Validation of model (4) is accomplished by utilizing an experimental setup of the pump-probe transient reflection measurements shown in Fig. 1. The output of amplified Titanium-Sapphire (Legend Eite, Coherent) laser was used as a source of fundamental laser radiation: wavelength 800 nm, pulse width 65 fs, pulse repetition rate 1 kHz, average power 2.5 W. The main part, 90%, of the radiation was converted into 350 nm by use of the optical parametric oscillator (Topas, Light Conversion) with additional second and fourth-harmonic generation and

was used as pump pulse. The remaining 10% was used to generate white light continuum in a rotating CaF_2 plate, i.e., the probe pulse [27].

Pump beam (fluence $\sim 40 \mu\text{J}/\text{cm}^2$) was focused on the surface of a $300 \mu\text{m}$ thick gold film deposited on a SiO_2 substrate with a focal length 30 cm lens and an incidence angle of 10° . Probe pulses with variable time delays relative to pump pulses were used to measure time-resolved transient reflection spectra and kinetics produced by the pump pulses. The full width at half maximum (FWHM) of the instrument response function was 100 ± 10 fs, which was obtained from the cross-correlation signal in quartz. According to previous studies [28, 29], the cross-correlation signal from quartz i.e. obtained from the so-called "coherent artifact", is a third-order nonlinearity process, and can be used to determine the temporal response function in ultrafast laser pump-probe measurements.

For direct comparison of the model with experimental data we use the normalized reflection change [5, page 119]. The maximal surface temperature, estimated from Eqn. (10) in [25], is 350 K. Hence, we are operating in the linear range of reflectivity versus the temperature [30, 31].

The dimensionless variable $\xi_p = 4.2 \cdot 10^{-3}$, Gold properties and their dependence on temperature can be found in the previous study [25].

Figure 2: Decay kinetics of the reflection changes at 520 and 600 nm from $300 \mu\text{m}$ gold plated quartz after the excitation with 350 nm laser pulse.

Fig. 2 shows comparison of the experimental results at the probe wavelength 520 nm and 600 nm with the developed model under variations of the radiation penetration depth. We found a good agreement between analytical model (4) and experimental results for the penetration depth of 8.0 nm and 3.5 nm, respectively, and phonon-phonon relaxation time $\tau = 12$ ps.

Let us denote the first and second integrals in (4) by $\theta_f(\xi)$ and $\theta_v(\xi)$, respectively. Contributions of $\theta_f(\xi)$ and $\theta_v(\xi)$ in the temperature response are different and depend on ξ_p and $\Delta\eta$. Note that, as a particular case, the dependence of the local temperature on $\theta_f(\xi)$ has been studied in [16]. Since, both the $\theta_f(\xi)$ and $\theta_v(\xi)$ functions are continuous and decreasing, their maximum values can be used to estimate each of those functions contributions to the entire solution. Let us compile a chart of the ratio of the $\max(\theta_v(\xi))$ to the $\max(\theta_f(\xi))$ as a function of ξ_p in the logarithmic scale as shown in Fig. 3. Since heat is dissipated in a surface layer of the gold film and it is assumed that the penetration depth can lie within the range between 2 nm and 10 nm. Therefore, values of $\Delta\eta$: 0.03, 0.075 and 0.15 shown in Fig. 3 are used to reflect the range of values of the penetration depth considered above. The space of the chart can be divided into two parts which are the top part (the value of the ratio is larger than one) defines the contribution of the term $\theta_v(\xi)$ and the bottom (the value of the ratio is less than one) defines the contribution of the term $\theta_f(\xi)$. Figure 3 shows that an increase of the value ξ_p tends to, on the one hand, decreasing the contribution of term $\theta_v(\xi)$ and, on the other hand, increasing the contribution of term $\theta_f(\xi)$ and vice versa when a decrease of the value of ξ_p occurs.

Figure 3: Analysis of contributions of functions, namely $\theta_f(\xi)$ and $\theta_v(\xi)$, to the entire solution. ξ_{p1}^v , ξ_{p2}^v and ξ_{p3}^v are left boundaries which correspond to $\Delta\eta=0.15$, 0.075 and 0.03, respectively.

As it can be seen from Fig. 3, all charts cross the axis which is passed through zero point of the axis of abscissa when the value of ξ_p is about one or in

algorithmic scale about zero. It means that contributions of both the $\theta_f(\xi)$ and the $\theta_v(\xi)$ terms are equivalent. Now, assuming that the value of ξ_p tends to zero the value of $\max(\theta_f(\xi))$ becomes small in comparison with the value of $\max(\theta_v(\xi))$ and model (4) can be simplified as:

$$\theta(\xi) \approx \theta_v(\xi) \quad (5)$$

Figure 4: Dependence of the left boundary ξ_p^v on $\Delta\eta$.

If the value of ξ_p tends to infinity, we have:

$$\theta(\xi) \approx \theta_f(\xi) \quad (6)$$

Hence, the three intervals of ξ_p can be defined as follows:

$$\begin{aligned} \text{I: } & (\xi_p < \xi_p^v), & \theta(\xi) & \approx \theta_v(\xi); \\ \text{II: } & (\xi_p^v < \xi_p < \xi_p^f), & \theta(\xi) & = \theta_f(\xi) + \theta_v(\xi); \\ \text{III: } & (\xi_p^f < \xi_p), & \theta(\xi) & \approx \theta_f(\xi), \end{aligned} \quad (7)$$

Where ξ_p^v and ξ_p^f are the left and right boundaries of intervals, respectively. The left boundary ξ_p^v and ξ_p is defined by the value of ratio the $\max(\theta_v(\xi))$ to the $\max(\theta_f(\xi))$ when its value becomes one order of magnitude greater than one. Similarly, the right boundary ξ_p^f and ξ_p is defined by the value of the same ratio but when its value becomes one order of magnitude less than one. The value of

the right boundary ξ_p^f can be defined directly from the chart (see Fig. 3) and to be about 6.15. Whereas, the value of the left boundary ξ_p^v is sensitive to $\Delta\eta$ and to define its value, the chart of dependence of ξ_p^v on $\Delta\eta$ can be used as it is shown in Fig. 4.

Figure 5: Temperature response cause of surface heat flux is denoted by broken curve. Temperature response cause of volumetric source is denoted by dashdot curve. Resulting profile of temperature response is denoted by firm curve.

Let us perform the numerical computations to display contributions of the transient heat flux and the volumetric heat source on surface temperature within defined intervals Eqn. (7). Figure 5 presents some results for the following

parameters: $\Delta\eta = 0.04$, and $\xi_p = 0.01, 1.10$, and 11.1 . As it is seen from Fig. 5, those results agree with Eqn. (7).

Thus, application of model (4) for the calculating transient heat transfer induced by ultra-short laser pulses can be proposed. At first the value of ξ_p is calculated (see Eqn. (12) in [25]). Then according to (7) the interval, in which ξ_p is situated, is defined. If value of ξ_p is within interval I or III the simplified model (5) or (6), respectively can be applied. Otherwise, both integrals the $\theta_f(\xi)$ and $\theta_v(\xi)$ must be taken into consideration to perform calculations (see model (4)).

4. Conclusion

We have studied the one-dimensional non-homogeneous hyperbolic energy equation within in a semi-infinite domain, and have applied to pump-probe femtosecond transient reflectance data. Obtained analytical model in the form of a Volterra-type integral equation which describes the surface temperature response of the thin film in ultrafast time scale takes into account contributions of the transient heat flux and the volumetric heat source. This model is validated by using experimental pump-probe transient reflectance data of a thin gold film with a time resolution of 50 fs. A good agreement between the experimental results and the theoretical model is found.

Moreover, the analysis of the obtained solution reveals that depending on parameters which are the FWHM of the laser pulse and penetration depth, the solution can be simplified in particular intervals of these parameters values. According to this analysis, the manner for the effective use of the obtained model is proposed.

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References

1. D. Cahill, W. Ford, K. Goodson, G. Mahan, A. Majumdar, H. Maris, R. Merlin, S. Phillpot, *J. Appl. Phys.* **93**, 793 (2003).
2. A. Dietzela, R. Bergera, P. Machtlea, M. Despontb, W. Haberleb, R. Stutzb, G. Binnigb, P. Vettigerb, *Actuat. A-Phys.* **100**, 123–130 (2002).

3. Y. Sun, D. Fangb, M. Sakaa, A. K. Soh, *Int. J. Solids Struct.* **45**, 1993–2013 (2008).
4. M. Ozisik, *Boundary value problems of heat conduction*, Dover Pubns, 2002.
5. D. Y. Tzou, *Macro to Microscale Heat Transfer: The Lagging Behavior*, Taylor & Francis, Washington, 1997.
6. S. Kakac, Y. Yener, *NASA STI/Recon Technical Report A* **86**, 21310 (1985).
7. X. Xu, C. Grigoropoulos, R. Russo, *J. Heat Trans.-T ASME* **117**, 17 (1995).
8. G. Chen, C. Tien, X. Wu, J. Smith, *J. Heat Trans.-T ASME* **116**, 325–331 (1994).
9. K. Goodson, M. Flik, *Appl. Mech. Rev.* **47**, 101 (1994).
10. V. V. Kulish, L. J. Lage, L. P. Komarov, P. E. Raad, *J. Heat Trans.-T ASME* **123**, 1133–1138 (2001).
11. V. V. Kulish, L. J. Lage, *J. Heat Trans.-T ASME* **122**, 372–376 (2000).
12. J. I. Frankel, *J. Thermophys. Heat Transfer* **20**, 945–949 (2006).
13. C. Cattaneo, *C. R. Acad. Sci.* **247**, 431–433 (1958).
14. P. Vernotte, *C. R. Acad. Sci.* **247**, 2103–2105 (1958).
15. D. Joseph, L. Preziosi, *Rev. Mod. Phys.* **61**, 41–73 (1989).
16. V. V. Kulish, B. V. Novozhilov, *Math. Probl. Eng.* **4**, 173–179 (2003).
17. S. Anisimov, B. Kapeliovich, T. Perel'man, *Sov. Phys. JETP* **39**, 375–80 (1974).
18. N. Singh, *Int. J. Mod. Phys. B* **24**, 1141–1158 (2010).
19. H. Inouye, K. Tanaka, I. Tanahashi, K. Hirao, *Phys. Rev. B* **57**, 11334–11340 (1998).
20. H. Hirori, T. Tachizaki, O. Matsuda, O. Wright, *Phys. Rev. B* **68**, 113102 (2003).
21. J. Chen, J. Beraun, *Numer. Heat Tr. A-Appl.* **40**, 1–20 (2001).
22. J. Chen, D. Tzou, J. Beraun, *International journal of heat and mass transfer* **49**, 307–316 (2006).
23. K. V. Poletkin, G. G. Gurzadyan, J. Shang, V. Kulish, *Appl. Phys. B* **107**, 137–143 (2012).
24. D. W. Tang, N. Araki, *J. Phys. D Appl. Phys.* **29**, 2527 (1996).
25. K.V. Poletkin, G.G. Gurzadyan, J. Shang, V. Kulish, *Appl. Phys. B* **107**, 137–143 (2012).
26. M. Abramowitz, I. Stegun, *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, US Government Printing Office, 2010.
27. J. Shang, Z. Luo, C. Cong, J. Lin, T. Yu, G. Gurzadyan, *Appl. Phys. Lett.* **97**, 163103 (2010).
28. B. Dietzek, T. Pascher, V. Sundström, A. Yartsev, *Laser Phys. Lett.* **4**, 38–43 (2007).

29. M. Lorenc, M. Ziolk, R. Naskrecki, J. Karolczak, J. Kubicki, A. Maciejewski, *Appl. Phys. B* **74**, 19–27 (2002).
30. J. Hohlfeld, D. Grosenick, U. Conrad, E. Matthias, *Appl. Phys. A-Mater* **60**, 137–142 (1995), 129th *WE-Heraeus-Seminar on Surface Studies by Nonlinear Laser Spectroscopies*, KASSEL, GERMANY, MAY 30-JUN 01, 1994.
31. J. Hohlfeld, J. Muller, S. Wellershoff, E. Matthias, *Appl. Phys. B-Lasers O.* **64**, 387–390 (1997).