International Journal of Heat and Mass Transfer 77 (2014) 17–21

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

Thermal properties of thin films studied by ultrafast laser spectroscopy: Theory and experiment

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ARTICLE INFO

Article history:
Received 19 February 2014
Received in revised form 23 April 2014
Accepted 23 April 2014
Available online 3 June 2014

Keywords:
Heat transfer
Ultrafast laser spectroscopy
Thermal properties
Thin films

ABSTRACT

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.

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, [4–6]). 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 [7–9]. 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] 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

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http://dx.doi.org/10.1016/j.ijheatmasstransfer.2014.04.054
0017-9310/

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 nonhomogeneous 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

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

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

$$\tau=\alpha/c^2, \tag{2}$$

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 Eq. (1), namely, the thermal diffusivity α, and the volumetric heat capacity C can be defined as for the bulk material.

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

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

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. [23]). For the surface temperature ($\eta = 0$), it becomes

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

where $I_0(\xi)$ is the modified Bessel function, $\delta(\xi)$ is the Dirac delta function, $erf(\xi)$ is the Gauss error function [25],

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

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 Eq. (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.

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

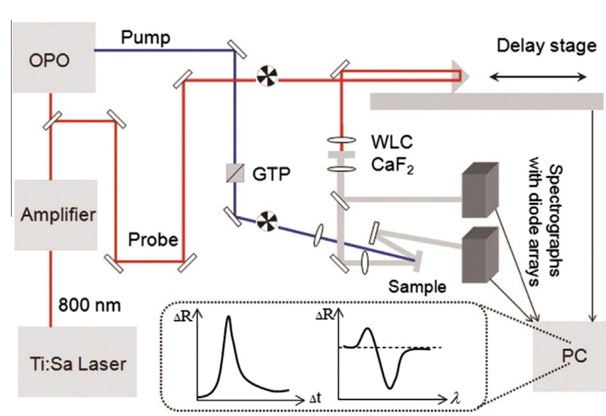

Fig. 1. Pump–probe setup: WLC (White Light Continuum); OPO (Optical Parametric Oscillator); GTP (Glan–Thompson Polarizer).