Manual for the use of the interface to compute the damage threshold of metals of various thicknesses following irradiation with femtosecond laser pulses

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Abstract

The employment of femtosecond pulsed lasers has received significant attention due to its capability to facilitate fabrication of precise patterns at the micro- and nano- lengths scales. A key issue for efficient material processing is the accurate determination of the damage threshold that is associated with the laser peak fluence at which minimal damage occurs on the surface of the irradiated solid. Despite a wealth of previous reports that focused on the evaluation of the laser conditions that lead to the onset of damage, the investigation of both the optical and thermal response of thin films of sizes comparable to the optical penetration depth is still an unexplored area.

The developed interface allows the evaluation of the impact of various parameters such as the photon energies and material thickness on the damage threshold for various metals (Au, Ag, Cu, Al, Ni, Ti, Cr, Stainless Steel) and at three different substrates (Si, SiO2 and soda lime silica glass). A multiscale physical model is used that correlates the energy absorption, electron excitation, relaxation processes and minimal surface modification.

I. THEORETICAL MODEL

To describe the damage induced on the material following irradiation with fs pulses, a theoretical framework is employed to explore the excitation and thermal response of a double-layered structure (thin metal film on a dielectric material). The simulation algorithm is based on the use of a Two Temperature Model (TTM) that represents the standard approach to evaluate the dynamics of electron excitation and relaxation processes in solids [1]. In this work, for the sake of simplicity, an 1D-TTM is used to describe the thermal effects due to heating of the thin films with laser pulses of wavelength λ_L for a pulse duration τ_p. It is noted that the solution of the TTM in 1D (along the energy propagation direction) is a standard approach used to describe thermal effects after irradiation of solids with femtosecond laser pulses [2, 3]. This is a reasonable choice assuming that, in principle, the laser spot radius is much larger (some tens of micrometers) than the thickness of the irradiated solid; therefore, the laser energy distribution along the lateral direction is considered uniform which means that the heat conduction along that direction is practically infinitesimal. Due to the presence of the substrate, the following set of rate equations is employed [4]

$$
\begin{aligned}
C_e^{(m)}\frac{\partial T_e^{(m)}}{\partial t} &= \frac{\partial}{\partial z}\left(k_e^{(m)}\frac{\partial T_e^{(m)}}{\partial z}\right) - G_{eL}^{(m)}\left(T_e^{(m)} - T_L^{(m)}\right) + S^{(m)} \\
C_L^{(m)}\frac{\partial T_L^{(m)}}{\partial t} &= \frac{\partial}{\partial z}\left(k_L^{(m)}\frac{\partial T_L^{(m)}}{\partial z}\right) + G_{eL}^{(m)}\left(T_e^{(m)} - T_L^{(m)}\right) \\
C_e^{(S)}\frac{\partial T_e^{(S)}}{\partial t} &= \frac{\partial}{\partial z}\left(k_e^{(S)}\frac{\partial T_e^{(S)}}{\partial z}\right) - G_{eL}^{(S)}\left(T_e^{(S)} - T_L^{(S)}\right) + S^{(S)} \\
C_L^{(S)}\frac{\partial T_L^{(S)}}{\partial t} &= \frac{\partial}{\partial z}\left(k_L^{(S)}\frac{\partial T_L^{(S)}}{\partial z}\right) + G_{eL}^{(S)}\left(T_e^{(S)} - T_L^{(S)}\right)
\end{aligned} \qquad (1)
$$

where the subscript 'm' (or 'S') indicates the thin film (or substrate). In Eqs.1, $T_e^{(m)}$ and $T_L^{(m)}$ stand for the electron and lattice temperatures, respectively, of the upper layer. The thermophysical properties of the metal such as the electron $C_e^{(m)}$ (or lattice $C_L^{(m)}$) volumetric heat capacities, electron $k_e^{(m)}\left(= k_{e0}^{(m)}\frac{B_e T_e^{(m)}}{A_e\left(T_e^{(m)}\right)^2 + B_e T_L^{(m)}}\right)$ heat conductivity, the electron-phonon coupling strengths $G_{eL}^{(m)}$, A_e, B_e and other model parameters that appear in the first two equations are listed in Table 1 (note A_g=194 Jm^{-3}K^{-1} for Cr). It is emphasised that as heat conduction in metals is, in principle, due to electrons, the thermal conductivity of the lattice is substantially smaller than that of the electron system. To include this large difference, $k_L^{(m)}$ is normally taken either equal to zero ($k_L^{(m)}$=0) [3, 5] or equal to a very small value compared to the electron heat conductivity ($k_L^{(m)}$=0.01$k_e^{(m)}$ is an expression that has been used in other reports [6, 7]). In this work and without loss of generality, we adopt the latter assumption.

The quantity $S^{(m)}$ represents the source term that accounts for the energy that the laser source provides to the metal surface which is sufficient to generate excited carriers on the thin film. As the purpose of the present investigation is to reveal the impact of optically excited *thin* films, it is important to take to into account the following processes: (i) a portion of the energy is absorbed from the material while part of the laser energy is transmitted into the substrate, (ii) the reflectivity and transmissivity of the irradiated material are influenced by a *multiple reflection process* between the two interfaces (air/metal and metal/substrate), (iii) the transmitted energy into the substrate is not sufficiently high to generate excited carriers and therefore, the third equation of Eqs.1 can be removed while the fourth can be simplified by $C_L^{(S)}\frac{\partial T_L^{(S)}}{\partial t}=\frac{\partial}{\partial z}\left(k_L^{(S)}\frac{\partial T_L^{(S)}}{\partial z}\right)$ where $T_L^{(S)}$, $C_L^{(S)}$, $k_L^{(S)}$stands for the substrate temperature, volumetric heat capacity and heat conductivity, respectively. The expression for the source term $S^{(m)}$ which is used to excite a metallic surface of thickness d is given from the following formula [5]

$$S^{(m)}=\frac{(1-R-T)\sqrt{4\log(2)}F}{\sqrt{\pi}\tau_p(\alpha^{-1}+L_b)}\exp\left(-4\log(2)\left(\frac{t-3t_p}{t_p}\right)^2\right)\frac{1}{(1-\exp(-d/(\alpha^{-1}+L_b))}\tag{2}$$

where R and T stand for the reflectivity and transmissivity, respectively, L_b corresponds to the ballistic length, α is the absorption coefficient that is wavelength dependent, and F is the peak fluence of the laser beam. The ballistic transport is also included in the expression as it has been demonstrated that it plays significant role in the response of the material [5]. Special attention is required for the ballistic length as in previous works, it has been reported that for bulk materials, L_b in *s/p*-band metals are comparable ($L_b^{(Au)}$=100 nm, $L_b^{(Ag)}$=142 nm, $L_b^{(Cu)}$=70 nm, $L_b^{(Al)}$=46 nm [5]) while for the *d*-band metals such as Ni, Ti, Cr, stainless steel, it is of the same order as their optical penetration depth [5]. It is noted that the above values of the ballistic length were used for λ_L~ 400-500 nm pulses [5, 8]. The photon energy of the laser beam is expected to influence the ballistic length of the electrons [9] and therefore, the use of the above values for L_b at higher wavelengths (i.e. 1026 nm) could be questionable. Nevertheless, in the absence of appropriate values for L_b at higher photon energies in bibliography, the above values for the ballistic length are used.

The calculation of R and T and the absorbance $A=1-R-T$ are derived through the use of the multiple reflection theory [10]. Thus, the following expressions are employed to calculate the optical properties for a thin film on a substrate (for a *p*-polarised beam)

$$R=|r_{dl}|^2,\quad T=|t_{dl}|^2Re(\tilde{N}_S),\quad r_{dl}=\frac{r_{am}+r_{mS}e^{2\beta j}}{1+r_{am}+r_{mS}e^{2\beta j}},\quad t_{dl}=\frac{t_{am}t_{mS}e^{\beta j}}{1+r_{am}+r_{mS}e^{2\beta j}},\quad \beta=2\pi d/\lambda_L\tag{3}$$

$$r_{CD}=\frac{\tilde{N}_D-\tilde{N}_C}{\tilde{N}_D+\tilde{N}_C},\quad t_{CD}=\frac{2\tilde{N}_C}{\tilde{N}_D+\tilde{N}_C}\tag{4}$$

where the indices $C=a,m$ and $D=m,S$ characterise each material (‘*a*’, ‘*m*’, ‘*S*’ stand for ‘air’, ‘metal’, ‘substrate’, respectively). The complex refractive indices of the materials such as air, metal and substrate are denoted with $\tilde{N}_a=1$, $\tilde{N}_m=Re(\tilde{N}_m)+Im(\tilde{N}_m)j$, $\tilde{N}_S=Re(\tilde{N}_m)+Im(\tilde{N}_m)j$. It is noted that a Drude-Lorentz model is used to obtain the dielectric function for each metal based on the analysis by Rakic *et* al. (where both interband and intraband transitions are assumed) [11]. As the optical parameters of an excited material does not remain constant during the excitation process [12], to introduce the transient change, a temporally varying expression of the dielectric function is provided by including a temperature dependence on the reciprocal of the electron relaxation time τ_e (i.e. $\tau_e=\left[A_e\left(T_e^{(m)}\right)^2+B_eT_L^{(m)}\right]^{-1}$) [13]. The values of the refractive indices of the metals in this study (at 300 K are given in Table 1).

The set of equations Eqs.1-4 are solved by using an iterative Crank-Nicolson scheme based on a finite-difference method. It is assumed that the system is in thermal equilibrium at t=0 and, therefore, $T_e^{(m)}(z,t=0)$=$T_L^{(m)}(z,t=0)=300$ K. A thick substrate is considered (i.e. $k_L^{(S)}\frac{\partial T_L^{(S)}}{\partial z}=0$) while adiabatic conditions are applied on the surface of the metallic surface (i.e. $k_e^{(m)}\frac{\partial T_e^{(m)}}{\partial z}=0$). Finally, the following boundary conditions are considered on the interface between the top layer and the substrate: $k_L^{(m)}\frac{\partial T_L^{(m)}}{\partial z}=k_L^{(S)}\frac{\partial T_L^{(S)}}{\partial z}, k_e^{(m)}\frac{\partial T_e^{(m)}}{\partial z}=0, T_L^{(m)}=T_L^{(S)}$.

	Material							
Parameter	**Au**	**Ag**	**Cu**	**Al**	**Ni**	**Ti**	**Cr**	**Steel (100Cr6)**
$\tilde{N}_m$	DL [11]	DL [11]	DL [11]	DL [11]	DL [11]	DL [11]	DL [11]	DL [13]
$G_{eL}^{(m)}$ [$Wm^{-3}K^{-1}$]	Ab-Initio [14]	Ab-Initio [14]	Ab-Initio [14]	Ab-Initio [14]	Ab-Initio [14]	Ab-Initio [14]	42×10^{16} [5]	Ab-Initio [15]
$C_e^{(m)}$ [$Jm^{-3}K^{-1}$]	Ab-Initio [14]	Ab-Initio [14]	Ab-Initio [14]	Ab-Initio [14]	Ab-Initio [14]	Ab-Initio [14]	$A_gT_e^{(m)}$ [5]	Ab-Initio [15]
$C_L^{(m)}$ [$\times10^6\, Jm^{-3}K^{-1}$]	2.48 [5]	2.5 [7]	3.3 [5]	2.4 [16]	4.3 [5]	2.35 [17]	3.3 [5]	3.27 [15]
$k_{e0}^{(m)}$ [$Wm^{-1}K^{-1}$]	318 [5]	428 [7]	401 [5]	235 [16]	90 [5]	21.9 [17]	93.9 [5]	46.6 [15]
A_e [$\times10^7\, s^{-1}K^{-2}$]	1.18 [7]	0.932 [7]	1.28 [7]	0.376 [16]	0.59 [7]	1 [17]	7.9 [6]	0.98 [15]
B_e [$\times10^{11}\, s^{-1}K^{-1}$]	1.25 [7]	1.02 [7]	1.23 [7]	3.9 [16]	1.4 [7]	1.5 [17]	13.4 [6]	2.8 [15]
T_{melt} [K]	1337 [18]	1234 [18]	1357 [18]	933 [18]	1728 [18]	1941 [18]	2180 [18]	1811 [18]

Table 1: Optical and thermophysical properties of materials (*DL* stands for Drude-Lorentz model).

It has to be emphasised that a more rigorous approach would also require the investigation of the impact of the electron (in the metal) – phonon (in the dielectric) scattering (EM-PD) heat transfer across metal-dielectric surfaces. More specifically, in previous reports, it has been shown that, especially for very thin films, the impact of EM-PD coupling increases at decreasing thicknesses and this phenomenon leads to remarkable variation in the relaxation process [19]. Thus, special emphasis on the role of the thermal resistance (related to the reciprocal of the EM-PD coupling) should be given. Nevertheless, in those studies, the use of approximate expressions both for the thermophysical and the optical parameters of the irradiated metals as well as the neglect of the relation of the optical parameters variation with thickness (i.e. application of the multiple reflection theory) do not allow a direct and consistent interpretation with experimental data. Furthermore, in those studies, a fitting approach through the use of appropriate experimental protocols was performed to estimate the thermal resistance. Thus, despite a non-vanishing EM-PD coupling, the evaluation of the associated thermal resistance is not straightforward. In this study, the incorporation of the role of thermal resistance on the thermal effects on the irradiated material has not been used; however, the evaluation of the damage threshold and comparison with experimental data are expected to function as a test for the need of a more complex (but, anyway, more consistent with the application of all underlying physical mechanisms).

A. STEPS TO PERFORM THE DAMAGE THRESHOLD EVALUATION

The user has to select, firstly,

a) the laser conditions (i.e. laser wavelength and pulse duration)
b) metal (type of metal and thickness)
c) substrate

a) the '**laser wavelength**' must be edited in '**nm**'. The range of the wavelength values of the laser beam that irradiates the metal is taken on data from paper of Rakic et al [11] (see also range in RefractiveIndex.INFO - Refractive index database considering the choice 'Rakic…'. In general, the wavelength range that has been tested so far for the purposes of this interface lie between 248 nm and 1500 nm.

IMPORTANT:

- ✓ for 'Steel', for two wavelengths ('515 nm', '1026 nm'), the optical properties of the material have already been incorporated into the model and no intervention from the user is required. For other laser wavelengths, the user has to enter: 'the real part of the refractive index' and the 'imaginary part of the refractive index (extinction coefficient)'
- ✓ For 'Silicon' substrate, for four wavelengths ('250 nm', '515 nm', '800 nm', '1026 nm') the refractive index of the substrate has already been incorporated and no intervention from the user is required. For other laser wavelengths, the user has to enter: 'the real part of the refractive index' and the 'imaginary part of the refractive index (extinction coefficient)'

The 'pulse duration' must be edited in 'fs'

b) Calculations can be currently performed for the class 'metal': 'Au', 'Ag', 'Cu', 'Al', 'Ni', 'Cr', 'Ti' and 'Steel' (100Cr6).

c) Three types of materials have been considered as 'Substrate': 'Silicon', 'Fused Silica' and 'Soda Lime Silica Glass'

I. METHODOLOGY

Given that the metal and substrate, thickness of the metal, wavelength and pulse duration of the laser pulse have been selected by the user, an initial value of the damage threshold (value that yields lattice temperatures just above the melting point) F^{test} is selected from the algorithm. A test is performed to evaluate whether the calculated lattice temperature on the surface of the material (maximum lattice temperature $T_L^{(max)}$) exceeds or not the melting point (T^{melt}). If $T_L^{(max)} > T^{melt}$ for F^{test}, then a reduced value of F_{new}^{test} is then used. If F_{new}^{test} leads to $T_L^{(max)} > T^{melt}$, further decrease of F_{new}^{test} is required. By contrast, if the new F_{new}^{test} leads to $T_L^{(max)} < T^{melt}$ then an intermediate value for the F_{new}^{test} is taken to represent the damage threshold. A similar procedure is followed if the initial value F^{test} leads to $T_L^{(max)} < T^{melt}$. In that case, an increment in the value of F_{new}^{test} is then performed and the above procedure is followed. It is noted that **all of the above steps do not require any intervention from the user**.

The execution of the algorithm takes into account both the thermophysical and optical parameter values of the irradiated complex (metal/substrate). It has been developed assuming the most common metals and substrates while it is aimed to be extended soon to other metals and configurations (multi-layered materials, etc). A minimal intervention is required from the user, mostly, to introduce the refractive index and extinction coefficient for Steel at wavelengths different from 515 nm and 1026 nm. The Similarly, the user is required to enter the refractive index and extinction coefficient for Silicon at wavelengths different from 250 nm, 515 nm 800 nm and 1026 nm (if it is used as a substrate).

II. OUTPUT

The text file that is produced (for example 'Results_Ni_SiO2_wavelength=1026nm_thickness=60nm.txt') has the following content:

Material:	Ni
Substrate:	SiO2
Wavelength (nm):	1026
Thickness (nm):	60
Damage Threshold (J/cm2):	0.12998
Discretization size (nm):	0.43333
Pulse duration (fs):	170
Maximum Temperature(K):	1728.0025
Damage point (K):	1728
Reflectivity (at 300K):	0.72299
Absorptivity (at 300K):	0.27701
Melting point (K):	1728

The 'Maximum Temperature' corresponds to the maximum temperature reached if the value 0.12998 J/cm2 is used. The closer this value to the 'Melting point' the better the accuracy of the code.

FURTHER ASSISTANCE

For more information on the theoretical model and the interface, read

1. [2206.08577] The impact of the substrate on the opto-thermal response of thin metallic targets following irradiation with femtosecond laser pulses (arxiv.org)
2. [2205.05342] Damage threshold evaluation of thin metallic films exposed to femtosecond laser pulses: the role of material thickness (arxiv.org)

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