Femtosecond Laser Pulse Train Effect on Optical Characteristics and Nonequilibrium Heat Transfer in Thin Metal Films

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The objective of this study is to numerically investigate the electron-phonon interactions and the nonequilibrium energy transfer in metal thin films irradiated by ultrashort pulse train lasers. In particular, the temporal and spatial variations in the optical properties during laser irradiation are discussed; the influence of the number of pulses per train and the pulse separation time are also examined. The present study uses the well-established two-temperature model to describe laser-solid interactions and the quantum approach to determine various properties such as electron heat capacity, electron thermal conductivity, collision frequencies, reflectivity, and absorption rates. It is found that as the number of pulses per pulse train increases, the nonequilibrium state between electrons and phonons gradually disappears because of the energy relaxation and the low electron thermal conductivity. The results show that the electron-electron and electron-phonon collision frequencies vary significantly with the number of pulses per train and the separation time per pulse, and that they considerably affect the reflectivity and absorption rate, in turn leading to a change in the ablation mechanism of thin metal films for pulse train laser heating.

Keywords: nonequilibrium energy transfer, pulse train lasers, ablation, ultrashort pulse laser, thin films

1. Introduction

Recently, ultrashort pulse train lasers have been attracting worldwide interest for industrial fabrication because lasers with pulse trains have advantages in micromachining and reducing the size of the undesirable heat-affected zone.¹⁻⁶) These advantages of pulse train laser heating in thin film structures have mainly been reported in experimental results over the past decade.¹⁻³) Nevertheless, the underlying energy transport mechanism for pulse train laser heating remains poorly understood. Moreover, researchers have widely used the two-temperature model (TTM) to clarify the electron-phonon energy transfer characteristics of thin film structures.⁶⁻¹²) In most research using the TTM, various properties have been assumed to be constant for the sake of simplicity. However, these assumptions may yield inaccurate results for laser-matter interactions, because some important properties such as electron thermal conductivity and collision frequencies vary substantially with temperature.¹¹⁻¹⁹) Thus, a more robust model is needed to analyze thermal and optical properties modulated by quantum effects over wide temperature ranges.

Tsai et al.⁵) studied pulse train laser heating of thin metal films and demonstrated nonequilibrium characteristics between electron and phonon temperatures using the TTM considering the quantum effects. They suggested that a different ablation mechanism would occur because the optical and thermal characteristics undergo considerable changes with the influence of pulse train lasers.⁵) Because they did not discuss the variations in optical and thermal properties during laser irradiation, it is difficult to account for the differences between the energy transport characteristics of pulse train lasers and those of single pulse lasers. Sim and Lee²⁰) investigated opto-energy phenomena in thin gold films heated by femtosecond pulse laser and showed that numerical prediction involving quantum effects was in better agreement with experimental data.

The ultimate goal of this study is therefore to investigate the electron-phonon interaction and the nonequilibrium energy transfer in gold thin films irradiated by ultrashort pulse train lasers using the well-established TTM. In particular, some relationships are used to yield improved prediction of electron heat capacity, electron thermal conductivity, collision frequencies, reflectivity, and absorption rates. In particular, the kinetic theory of hot plasma and cold solids is used in determining collision frequencies, and it predicts variations in reflectivity and absorption rates. The electron heat capacity is also obtained from the Fermi-Dirac distribution. The electron thermal conductivity is calculated using the Drude theory. In particular, the laser absorption mechanism and the nonequilibrium energy transfer of pulse train lasers are discussed in terms of the numerical results, and the influences of the number of pulses per pulse train and pulse separation time on the optical and thermal properties are further examined.

2. Theoretical Background and Numerical Methods

Under ultrashort pulse laser irradiation, the spatial and temporal evolutions of the electron and lattice temperatures can be described by the following energy equations:²¹,²²)

\[ C_e(T_e) \frac{dT_e}{dt} = \nabla [k_e(T_e) \nabla T_e] - G(T_e - T_l) + S(z,t) \quad (1) \]

\[ C_l(T_l) \frac{dT_l}{dt} = G(T_e - T_l) \quad (2) \]

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where $C$ is the heat capacity with respect to temperature, $k_e(T_e)$ is the electron thermal conductivity, the subscripts $e$ and $i$ stand for electron and lattice, respectively, $G$ is the electron-phonon coupling factor, and $S(z,t)$ represents the laser heating source term. In eq. (3), $R(0, i)$ denotes the reflectivity at the surface, $J$ is the laser fluence, $t_p$ is the pulse duration, and $\alpha(r, t)$ is the absorption coefficient.

On the basis of the melting temperature and the Fermi temperature, three different regimes are considered to determine the electron-electron and electron-phonon collision frequencies. First, for the hot plasma regime, where the electron temperature is comparable to or larger than the Fermi temperature, the electron collision frequency highly associated with optical properties can be expressed in terms of the Coulomb collision frequency and the electron temperature as \cite{14,23}

$$v = k_e \frac{Z n_e \ln A \Lambda}{T_e^{3/2}},$$

where $Z$ is the ionization degree, $n_e$ is the electron number density, and $\ln A$ indicates the Coulomb logarithm.

The electron-phonon collision frequency is proportional to the phonon temperature for electron temperatures lower than the melting temperature. Thus, the collision frequency can be defined as \cite{33}

$$v = k_e \left( \frac{m_e}{M} \right)^{1/2} \frac{J_i}{\hbar} \frac{T_i}{T_d},$$

where $M$ represents the ion mass, $m_e$ is the electron mass, $J_i$ is the ionization potential, $\hbar$ is the reduced Planck constant, and $T_d$ is the Debye temperature. By matching with the measured reflectivity $R = 0.93$ of gold at room temperature, the collision frequency of this regime can be estimated to be about $8.5 \times 10^{14}$, yielding a numerical constant $k_e$ of 11.3.

The present study also establishes an intermediate regime through the interpolation of the electron mean free path and the electron velocity between the hot plasma and the cold solid regimes, as indicated previously. In this regime, the mean free path of electron can be expressed as \cite{43}

$$\lambda_e > r_0 = \left( \frac{3}{4\pi n_i} \right)^{1/3},$$

where $r_0$ is the ion sphere radius and $n_i$ represents the ion number density. The collision frequency in the intermediate regime can be determined from Ref. 14) to be

$$v = k_e \frac{V_e}{r_0},$$

where $V_e$ is the velocity of electron. In eqs. (4), (5), and (7), a numerical constant, $k_e$, is determined from experimental data and the interfacial condition for each regime. Furthermore, the dielectric function and the complex refractive index are determined using the Drude model, and they are used for estimations of the reflectivity and the absorption coefficient. For metal, the dielectric function consists of two parts, \cite{24}

$$\varepsilon_1 = 1 - \frac{\omega_p^2}{\omega_p^2 + \nu^2},$$

$$\varepsilon_2 = \frac{\nu \omega_p^2}{\omega_p^3 + \nu^2 \omega_p},$$

where $\varepsilon_1$ represents the real part of the dielectric function, $\varepsilon_2$ is the imaginary part of the dielectric function, $\omega_p$ is the plasma frequency, $\omega_p$ is the laser frequency, and $\nu$ represents the collision frequency. The complex refractive index of metal can be expressed as \cite{24}

$$n = \sqrt{\frac{\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}}{2}},$$

$$k = \sqrt{\frac{-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}}{2}},$$

where $n$ is the refractive index and $k$ represents the extinction coefficient. Ultimately, the reflectivity and the absorption coefficient at normal incidence can be derived using the Fresnel equations \cite{24}

$$R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2},$$

$$\alpha = \frac{4\pi k}{\lambda},$$

where $\lambda$ is the wavelength of the incident laser. Meanwhile, the electron thermal conductivity is determined using Drude theory \cite{18,19} to be

$$k_e(T_e) = \frac{1}{3} C_e(T_e) V_e^2(T_e) \tau_e(T_e),$$

where $\tau_e$ is the electron relaxation time with respect to the electron temperature. The present study estimates the electron heat capacity on the basis of the Fermi temperature \cite{18,19}. For electron temperatures higher than the Fermi temperature, the electron heat capacity can be estimated as \cite{18,19}

$$C_e = \frac{3}{2} n_e k_B,$$

where $k_B$ is the Boltzmann constant. For $T_e < T_F$, on the other hand, the electron heat capacity can be described as \cite{18,19}

$$C_e = \gamma T_e,$$

where $\gamma$ is the electron heat capacity constant as determined from the experimental data.

The finite difference method with a fully implicit scheme is adopted for the discretization of the governing equations. Integration of the transient terms is employed over the control volume and over a time interval from $t$ to $t + \Delta t$ as follows:

$$\int_t^{t+\Delta t} \int_{CV} \frac{\partial \rho}{\partial t} dV dt \approx (C_P \phi_P - C_V \phi_P^0) \Delta V,$$

where $CV$ means the control volume, $\phi$ refers to the particle’s temperature and the carrier number density, $N$. The super-
script 0 represents old value at \( t \). In addition, the diffusion terms are discretized with the second-order central differencing scheme. Moreover, in order to clarify the stability of the final solutions, the present study examines the sensitivities of time step and mesh size. Finally, numerical solutions are obtained when the residuals from the governing equations are less than \( 10^{-4} \) for gold films.

A 200-nm-thick gold film is used and, following Ref. 19), the initial electron number density is set to \( 5.9 \times 10^{28} \text{ m}^{-3} \). The initial electron and lattice temperatures are taken to be 300 K for a pulse duration of 140 fs. The total laser fluences considered are 0.16 J/cm\(^2\) and 0.2 J/cm\(^2\). In order to see the influence of the number of pulse per train for a single burst on the laser-solid interactions, this study uses four different numbers of pulses, 1, 2, 5, and 10. Moreover, the present study conducts numerical simulations for pulse separation times of 1, 2, 4, 5, 8, and 10 ps, in order to clarify the separation time effect on the energy transport. Neumann boundary conditions are applied at the top and bottom surfaces of the thin film structure. The physical properties of the gold film are listed in Table 1.

### Table 1 Physical properties of gold used in this simulation.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron number density</td>
<td>( 5.9 \times 10^{28} \text{ m}^{-3} )</td>
<td>18</td>
</tr>
<tr>
<td>Electron heat capacity constant</td>
<td>( 6.7 \times 10^{-4} \text{ J/mol-K} )</td>
<td>19</td>
</tr>
<tr>
<td>Ion mass</td>
<td>196.97 [a.m.u]</td>
<td>19</td>
</tr>
<tr>
<td>Debye temperature</td>
<td>170 [K]</td>
<td>19</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>1337 [K]</td>
<td>19</td>
</tr>
<tr>
<td>Fermi temperature</td>
<td>( 6.39 \times 10^4 \text{ [K]} )</td>
<td>18</td>
</tr>
<tr>
<td>First ionization potential</td>
<td>9.22 eV</td>
<td>18</td>
</tr>
</tbody>
</table>

3. Results and Discussion

Figure 1 shows the temporal distributions of the electron and lattice phonon temperatures at the top surface irradiated by a single burst laser with different numbers of pulses at a total fluence of 0.21 J/cm\(^2\). The pulse duration and the laser wavelength were set to 140 fs and 1053 nm, respectively. The separation time was defined as the time interval between two pulses, and 1.0 ps was used for four cases. The peak value of the electron temperature increased gradually because of the incubation effect, indicating that successive absorption occurred in the materials during the laser pulses. It was found that the maximum electron temperatures decreased with the increase in the number of pulses, indicating that even if the total laser fluences were the same for all cases, the laser intensities absorbed at the top surface for each pulse can vary substantially with the number of pulses, because the pulse train lasers affect the change in the optical properties, and the heated electrons release their absorbed energy to electrons and phonons during the separation time. Furthermore, the nonequilibrium state between electrons and phonons gradually disappeared as the number of pulses per pulse train increased because, even for the same total fluence, the laser intensity at each pulse decreased as the number of pulses increased, and the electron thermal conductivities were reduced relative to a single pulse.

![Fig. 1 The estimated temporal profiles of the electron and phonon temperatures at the top surface with a total fluence of 0.21 J/cm\(^2\).](image-url)
Figure 2 depicts the transient variations in reflectivity and laser intensity at the top surface for the single and two-pulse trains. In both cases, the reflectivity at the early stage of laser exposure decreased considerably because the collision frequencies and the dielectric functions changed with an abrupt increase in electron temperature during laser irradiation with high peak power and a very short pulse. Figure 2(b) shows that the effective laser intensity of the first pulse was lower than that of the second pulse because of the decrease in reflectivity from 93 to 75% during laser irradiation. It indicates that, prior to the second pulse, the film properties had already changed due to the heating by the first pulse. This change is demonstrating that the optical characteristics for pulse train laser are different from that using the single pulse laser, and in turn, the decrease in reflectivity can increase the absorption of photon energy and affect the ablation process in thin films.

Figure 3 shows the electron thermal conductivity at the top surface during the ultrashort pulse train laser heating of the thin gold film with a pulse duration 140 fs. No substantial difference was seen between the five-pulse and the single-pulse cases. However, in the ten-pulse case, the electron thermal conductivity was much lower at the early stage of laser irradiation because the electron temperature decreased dramatically with increasing number of pulses, as shown in Fig. 1. The decrease in electron thermal conductivity makes it possible to mitigate the thermal problem. On the other hand, it was found that as the number of pulses increased, the electron thermal conductivity remained high for an extended time compared to that of the single-pulse case due to the incubation effect.

Figure 4 plots the spatial distribution of the lattice phonon temperature with respect to the number of pulses. In all cases, the pulse duration and the total laser fluence were 140 ps and 0.2 J/cm², respectively. The lattice temperature at 25 ps increased with the number of pulses in all cases. This is because the absorption rate for the pulse train laser was greater than that for a single pulse (see Fig. 5) and also because the incubation effect plays an important role in increasing the lattice temperature. The estimated spatial distribution of the absorption coefficient at 25 ps is depicted in Fig. 5. It turns out that the absorption coefficient increased slightly with the number of pulses, which is strongly associated with the dielectric function. Therefore, because of the different laser intensities at each pulse, the absorption rate of the thin film structure irradiated by the pulse train laser was somewhat greater than that of the single pulse.

Figure 6 demonstrates the influence of pulse separation time in a pulse train laser consisting of four pulses of 0.04 J/cm², as determined by the pulse separation technique. The present study extensively simulates the temporal responses of the electron and phonon temperatures for separation times of 1, 2, 5, and 10 ps. It is clear that as the separation time increases, the equilibrium time decreases. For instance, the equilibrium time was estimated to be 10 ps to 15 ps at tₚ = 1 ps and 2 ps, whereas it was predicted to be 5 ps for 5 ps and 10 ps. Our results will be helpful in determining the optimal conditions for micromachining by controlling the separation time. In fact, the separation time affects the lattice temperature and the optical properties such as the dielectric function and the complex refractive index. Moreover, the incubation effect for the pulse train decreases with increasing pulse separation time, because heated electrons transfer their energy to phonons.

Meanwhile, the temporal variation in reflectivity with respect to various pulse separation times is plotted in Fig. 7.
As the separation time increased, the reflectivity changed considerably because of the energy transfer between electrons and phonons and the variation in collision frequency. The separation time would be one factor which reduces the extent of the nonequilibrium state. When the separation time was shorter than the equilibrium time, the reflectivity values estimated for cases (a) and (b) were nearly the same, as shown in Fig. 7(a), whereas for separation times comparable or longer than the equilibrium time, those values were substantially different from one another, because of the energy relaxation between electrons and phonons.

4. Conclusions

This article reports a numerical investigation of the effects of a femtosecond pulse train laser on the optical characteristics and the nonequilibrium energy transport in thin gold film structures using TTM to consider the quantum effects. The influence of the number of pulses per pulse train and the separation time was extensively discussed and is summarized below.

(1) It was confirmed that the optical characteristics of pulse train lasers differ from those of single-pulse lasers, and the nonequilibrium energy transfer varies with the number of pulses per train. As the number of pulses increases, the number of peaks for electron temperature increases, and the maximum electron temperature increases due to both the incubation effect and the increase in absorption rate. It was also found that the reflectivity at the surface undergoes a significant transition due to heating from the first pulse.

(2) The absorption rate tends to be greater for pulse train lasers than for single-pulse lasers. This may be useful in improving the efficiency of micromachining by controlling the number of pulses. In addition, the electron thermal conductivity for ten pulses per train is lower than that of the single pulse during the early stage of laser irradiation because of the lower electron temperature for a train of ten pulses. This makes it possible to reduce the size of the heat-affected zone. Even if the laser irradiation is terminated, the electron thermal conductivity remains high because of the effect of...
incubation on the electron temperature, unlike for the single-pulse laser. This reveals that ultrashort pulse train lasers have advantages for micromachining when compared to single-pulse lasers.

(3) As the separation time increases, the equilibrium time decreases. Also, the effect of incubation on the pulse train decreases with increasing pulse separation time because the heated electrons transfer their energy to the phonons. It was found that as the separation time increases, the reflectivity changes considerably due to the energy transfer between electrons and phonons and the variation in the collision frequency. The separation time is one factor that reduces the extent of the nonequilibrium state. When the separation time is shorter than the equilibrium time, the reflectivities are nearly the same, whereas when the separation time is comparable to or longer than the equilibrium time, the reflectivities are different from each other because of the energy relaxation between the electrons and phonons.
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REFERENCES


Nomenclature

$C_e$: electron heat capacity [J/m$^3$K]
$C_l$: lattice heat capacity [J/m$^3$K]
e: electron
$I$: laser intensity [W/m$^2$]
k: extinction coefficient
$k_e$: electron thermal conductivity [W/mK]
$k_B$: Boltzmann constant [J/K]
k_n: numerical constant
$G$: electron-phonon coupling factor [W/m$^3$K]
h: reduced Planck constant [Js]
$J$: laser fluence [J/cm$^2$]
$J_0$: first ionization potential [eV]
l: lattice
$M$: ion mass [kg]
$m_e$: electron mass [kg]
n_i: ion number density [/m$^3$]
$n_n$: electron number density [/m$^3$]
n: refractive index
$\rho_i$: ion sphere radius [m]
$R$: reflectivity
$S$: laser heating source term
$t$: time [s]
$t_p$: pulse duration [s]
$T$: temperature [K]
$T_D$: Debye temperature [K]
$T_F$: Fermi temperature [K]
$T_e$: electron temperature [K]
$T_l$: lattice temperature [K]
$V_e$: electron velocity [m/s]
v: collision frequency [/s]
$Z_\text{ion}$: ionization degree
$n_p$: the number of pulses per pulse train
$t_s$: pulse separation time [s]
$\alpha$: absorption coefficient
$\gamma$: the electron heat capacity constant [J/molK]
$\varepsilon_1$: real part of the dielectric function
$\varepsilon_2$: imaginary part of the dielectric function
$\lambda$: laser wavelength [m]
$\lambda_{m}$: electron mean free path [m]
$\ln A$: Coulomb logarithm
$\omega$: laser frequency [/s]
$\omega_p$: plasma frequency [/s]