Simulation of the thermionic emission during ultrashort pulse laser ablation of metals

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Abstract. The characteristics of thermionic emission of metal films during ultrashort pulse laser ablation are investigated by numerical simulation. The two-temperature model is used to calculate the electron and lattice temperatures while thermionic emission is incorporated into the model as a surface phenomenon. The Richardson-Dushman equation is employed to estimate the rate of thermionic electron emission. The influence of laser irradiance and the film thickness on the emission rate is examined. The change of quantum efficiency is predicted and compared with reported experimental data. The evolution of electron and lattice temperatures and the variation of relaxation time are also investigated in accordance with thermionic emission.

1. Introduction
Electron emission during ultrafast laser ablation is an important phenomenon that influences the thermal behavior of the target and also the laser-induced plasma. It was reported that thermionic emission (TE) is the dominant mechanism for electron emission during femtosecond laser ablation of metals for the laser fluence range of 0.7-1.1 mJ/cm² [1]. Due to the extremely short time scale, the electron emission by femtosecond laser ablation is a candidate for the development of pulsed, high-current, electron beam source for the application to x-ray source [2], electron accelerator, free electron lasers [3], and so forth. In spite of the potential importance, the electron emission characteristics during ultrafast laser ablation have received much less attention compared to subjects like energy relaxation between electrons and phonons or the surface morphology of an ablated substrate. The electron emission during ultrashort pulse laser ablation of semiconductors was investigated by Mao et al. for picosecond pulse [4] and by Lobzenko et al. [5] for the effect of TE on laser energy absorption. More recently, the dependence of TE on peak laser intensity was reported for femtosecond laser ablation of molybdenum [6].

In this work, we report the results on numerical simulation of TE of metal films during femtosecond laser ablation. We used the two-temperature model (TTM) to calculate the temperature of the film and the Richardson-Dushman equation to estimate the TE rate. The variation of the electron emission rate with respect to the laser beam irradiance, the process parameter, and to thickness of the film, the target parameter, is investigated. The change of quantum efficiency for these parameters is estimated and compared with the reported experimental data.
2. Theoretical model

2.1 Thermionic emission

If the temperature of the conduction electrons in a metal is high enough, the tail part of the Fermi-Dirac distribution leaks into the vacuum level, resulting in the thermionic electron emission. The rate of TE from metal, \( N \), is represented by the Richardson-Dushman equation \[1,7\]

\[
N = \frac{A_0}{e} T_e^2 \exp \left(-\frac{e\phi}{k_B T_e}\right)
\]

where \( T_e \) is the electron temperature, \( \phi \) is work function, \( e \) is the charge of an electron, \( k_B \) is the Boltzmann constant. The constant \( A_0 \) is expressed by

\[
A_0 = \frac{4\pi m e^2 k_B^2}{h^3} = 1.2 \times 10^6 \text{ amp/m}^2 \cdot \text{K}^2
\]

where \( m \) is the mass of an electron and \( h \) is the Planck constant. The Richardson-Dushman equation in Eq. (1) is applicable for the condition at which the Fermi energy is approximately equal to the chemical potential. For metals, this condition is satisfied if \( k_B T_e \) is below 1 eV as noted in Ref. [1].

2.2 Two-Temperature Model

The TTM has been widely used to theoretically predict ultrafast laser ablation phenomena and to explain experimental data. For laser ablation of metals with subpicosecond pulses, the incident photon energy is first absorbed by the free electrons which as a consequence reach a highly non-equilibrium state. The excited electrons then quickly establish a thermal equilibrium by collisions within on the order of several hundred femtoseconds which decreases with increasing excitation level [8,9]. Once thermal equilibrium is established among the electrons, the energy distribution from hot electrons to lattice occurs through electron-phonon interactions. The characteristic time scale for the electron-phonon energy transfer, known as thermalization time, ranges from sub-picosecond to a few picoseconds for low fluences depending on the material. Therefore, the analysis of thermal state of a metal target irradiated by an ultrashort laser pulse requires that the electron temperature and lattice temperature be considered separately.

In TTM, the electron and lattice temperatures are expressed by the following equations.

\[
C_e(T_e) \frac{\partial T_e(z,t)}{\partial t} = \frac{\partial}{\partial z} \left( k_e(T_e) \frac{\partial T_e(z,t)}{\partial z} \right) - G(T_e(z,t) - T_l(z,t)) + S(z,t)
\]

(2)

\[
C_l \frac{\partial T_l(z,t)}{\partial t} = G(T_l(z,t) - T_e(z,t))
\]

(3)

where \( C \) is the specific heat capacity, \( z \) is the distance measured from the surface into the film, \( t \) is time, \( k \) is thermal conductivity and the subscripts \( e \) and \( l \) denote the electron and phonon, respectively. The temperature dependent \( C_e \) and \( k_e \) are given by \( C_e(T_e) = \gamma T_e \) and \( k_e(T_e) = k_{eq}(T_e/T_l) \) where \( \gamma \) is the electron heat capacity and \( k_{eq} \) is the electron thermal conductivity at thermal equilibrium. \( G \) is the electron-phonon coupling constant. The source term \( S \) represents the absorbed energy and expressed by

\[
S(z,t) = -\frac{dI(z,t)}{dz} = (1-R)I_0 \exp \left[-\frac{\left|t-t_0\right|^2}{(0.5\tau_p)^2}\right] \alpha \exp(-\alpha z)
\]

(4)

where \( I_0 \) is the laser irradiance, \( R \) is the surface reflectance, \( \alpha \) is the absorption coefficient of the metal film, \( \tau_p \) is pulse width at \( 1/e \) of the peak irradiance, and \( t_0 \) is the time at which the peak intensity is located.

In the present model, TE is incorporated into the boundary condition of the TTM as

\[
k_e \frac{\partial T_e(0,t)}{\partial z} = (E_f + e\phi)N
\]

(5)

where \( E_f \) is Fermi energy of the metal. In Eq. (5), \( E_f + e\phi \) is the potential barrier for an electron to be removed from the metal. The kinetic energy of the outgoing electrons is ignored. At \( z = d \), the boundary
condition, $\partial T_e (d,t) / \partial z = 0$, is applied.

Since the emission of electrons at the surface will cause a gradient in the electron number density, denoted by $n$, we also calculated the diffusion of electrons within the film using the diffusion equation

$$\frac{\partial n}{\partial t} = D_e \frac{\partial^2 n}{\partial z^2}$$

(6)

where $D_e$ is electron diffusion coefficient. Because of the lack of information for $D_e$, we derived $D_e$ as follows. The mobility of electrons in a conducting medium under an electric field $E$ is represented by

$$\mu_e = |v|/E,$$

where $v$ is the drift velocity described by $v = eE\tau_e / m$ [10]. Since both diffusion and mobility are statistical thermodynamic phenomena, $D_e$ and $\mu_e$ are not independent to each other but related by the Einstein relation as

$$\frac{D_e}{\mu_e} = \frac{k_B T_e}{e}$$

(7)

Using Eq. (7), $D_e$ was calculated with the electron relaxation time $\tau_e = 3m e q / \pi^2 n_k^2 T_e$ [12]. The boundary conditions of Eq. (6) are $D_e \partial n(0,t) / \partial z = N_e$, $\partial n(d,t) / \partial z = 0$. The ballistic transport of electrons was not considered in our model.

The Eqsns. (2), (3) and (6) are solved numerically using the explicit finite difference method.

### 3. Results and Discussion

For the calculation, we assumed a Gaussian pulse with $t_p = 200$ fs. To minimize the abrupt energy incidence and termination, we used a sufficiently long pulse with $t_0 = 700$ fs. For the target material, gold is selected because of its relatively well known thermal and optical properties. The material properties of gold include $R = 0.48$ [13] and $\sigma = 6.524 \times 10^7$ m$^{-1}$, $\gamma = 71$ Jm$^{-3}$K$^{-2}$, $k_w = 318$ Wm$^{-1}$K$^{-1}$ [9], $C_f = 2.5 \times 10^6$ Jm$^{-3}$K$^{-1}$ [14]. Recently, Jiang et al. [12] reported that the TTM predicts a higher damage threshold of gold films than experimental results unless full-run quantum treatments are employed for temperature-sensitive properties like $C_e$ and $k_e$. They suggested $0.1 T_f$ as the limit of electron temperature to apply the TTM without full-run quantum treatment, where $T_f$ is the Fermi temperature ($5.9 \times 10^4$ K for gold). Considering this limit and the condition for Richardson-Dushman equation as explained in Section 2, we limited our calculation for laser irradiances at which the maximum electron temperature does not exceed 10,000 K.

The electron-phonon coupling constant $G$ is a key factor influencing the development of electron and lattice temperatures and thus the accuracy of calculation results. From reflectance measurement of gold films, Hohlfeld et al. [9] reported $G = (2.2 \pm 0.3) \times 10^{16}$ Wm$^{-3}$K$^{-1}$ as the optimum value and also provided a summary of $G$ values in literature that vary more or less around $2.0 \times 10^{16}$ Wm$^{-3}$K$^{-1}$. Accordingly, we used $G = 2.0 \times 10^{16}$ Wm$^{-3}$K$^{-1}$ for the present study. The work function and Fermi energy of gold film are 4.3 and 5.53 eV, respectively [15]. $D_e$ was calculated using Eq. (7) and for simplicity a constant value of 0.005 m$^2$s$^{-1}$ that corresponds to the room temperature condition is used. Also, $T_e(z,0) = T_l(z,0) = 273$ K and $n(z,0) = 5.9 \times 10^{28}$ m$^{-3}$ [Jiang 12] were used for the initial conditions.

Figure 1 shows the variation of $T_e$ and $T_l$ at the surface with and without TE for a 20 nm thick gold film. It is clear that TE can lead to a significant difference in the electron and lattice temperatures during ultrashort pulse laser ablation. With TE, the system temperature at thermal equilibrium is 1313 K, below the melting temperature ($T_m = 1337$ K [12,16]). Conversely, when TE is not considered, the lattice temperature reaches $T_m$ before thermal equilibrium that is established at 1618 K. The differences in $T_e$ and $T_l$ between with and without TE cases are more pronounced for thinner films or for higher laser energy conditions.

Figure 2 shows the temporal change of electron emission flux due to TE with respect to laser irradiance for $d = 100$ nm. When the area under each curve is integrated, the total number of thermionic electrons per unit area per pulse ($N_{pulse}$) is obtained. Since the emission flux does not go to zero unless $T_e$ is zero, see Eq. (1), the duration of TE, emission time, is defined by $T_e = T_{0.8 N} - t_0$, where $T_{0.8 N}$ is the
instance at which the accumulated number of thermionic electrons reach 0.8\times N_{pulse}. The emission time is shown in figure 3 with the thermalization time, $\tau_t$. For low laser irradiances, the emission time is almost the same order as the laser pulse and increases only to \sim 5 \text{ ps} at $I=23\times10^{10}$ W/cm$^2$, indicating the possibility that electron pulses of picosecond width can be produced through TE induced by ultrashort pulse laser ablation. Note, however, that although most of the electrons are emitted during or immediately after the pulse, the tail portion of the emission profiles in figure 2 is much longer than $\tau_{em}$. The thermalization time also increases with irradiance. For low irradiance, $\tau_t$ shows no difference between with and without TE cases. However, at higher irradiances, $\tau_t$ with TE becomes shorter than that without TE due to the energy loss through TE.

Figure 4 shows the $N_{pulse}$ as a function of laser irradiance. Using these data, we can estimate the quantum efficiency ($\eta$), defined as the ratio of thermionic electrons to laser photons, as in figure 4. For the calculation of $\eta$, laser wavelength of 800 nm was used. We compare these data with the experimental data by Egbert et al. [2] which are for TE of molybdenum during ablation with 120 fs pulse and 780 nm wavelength. In Ref. [2], it was reported that the quantum efficiency measured for variable pulse energy and pulse width fits into a single curve expressed as a function of irradiance, that is, $\eta_{exp}=6\times10^{-8}\exp(-1.8\times10^{11}/I)$ which is also plotted for comparison in figure 4.

The calculated quantum efficiency ($\eta_{num}$) of the present study significantly overestimates the experimental data. Also, unlike the experimental data that show a saturation of emission flux, the $\eta_{num}$ continues to increase with laser irradiance. Despite these discrepancies between $\eta_{exp}$ and $\eta_{num}$, the calculation results are still informative in the sense that its profile is very similar to the experimental one. Furthermore, the threshold irradiance for TE agrees well between them. The reasons for the observed difference between $\eta_{exp}$ and $\eta_{num}$ may be due to i) the difference in materials, gold and
molybdenium, for which not sufficient experimental results are available for comparison ii) the space-charge (SC) effect, and iii) the kinetic energy (KE) of emitted electrons. The space-charge effect arises due to the Coulombic interaction among the emitted electrons when those are still in the vicinity of the surface. Riffe et al. [1] reported that the SC effect tends to drive the later-escaping electrons back to the surface, producing an experimental yield far less than the theoretical one. To overcome this SC effect, the electrons may need substantial KE to eventually leave the surface. The inclusion of electron kinetic energy into the model will lead to a decrease in the electron temperature, which will in turn reduce the emission rate described by Eq.(1).

The maximum value of $\eta_{exp}$ in figure 4 is about $10^{-7}$. Noting that $\eta$ does not go to zero, the threshold irradiance for TE is defined as $\eta_{th}=0.01\eta_{exp,max}$, which leads to $I=3\times10^{16}$ W/cm$^2$ as the threshold irradiance for 100 nm thick gold film.

The variation of $N_{pulse}$ with respect to film thickness is also examined for $d=20-300$ nm at $I=9\times10^{10}$ W/cm$^2$. $N_{pulse}$ drops exponentially from $5.8\times10^{14}$ to $1.3\times10^{11}$ as $d$ increases from 20 to 150 above which it remains almost the same at $1.2\times10^{11}$. The corresponding change of quantum efficiency ranges from $8\times10^{-3}$ to $1.6\times10^{-6}$. Thus, in the TE point of view, a film with $d\geq150$ nm may be regarded as a bulk metal.

Temporal variation of electron number density inside the film showed that the density gradient is most significant immediately after the pulse and near the surface. Although the density gradient gradually decreases with time, an appreciable gradient was maintained approximately for the emission time.

4. Conclusion
The characteristics of thermionic emission of gold films during ultrashort pulse laser ablation are investigated using TTM coupled with the Richardson-Dushman equation. It is found that TE can significantly change the development of electron and lattice temperatures, especially for thin films and at high irradiances. The short emission time implies that TE can be a useful source for picosecond scale electron pulse. Although the TTM overestimates the TE rate, it produces qualitatively similar data to the experimental ones and SC effect should be considered for improvement.

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