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Space charge limited electron emission from a Cu surface under ultrashort pulsed laser irradiation

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In this theoretical study, the electron emission from a copper surface under ultrashort pulsed laser irradiation is investigated using a one-dimensional particle in cell model. Thermionic emission as well as multiphoton photoelectron emission were taken into account. The emitted electrons create a negative space charge above the target; consequently the generated electric field reduces the electron emission by several orders of magnitude. The simulations indicate that the space charge effect should be considered when investigating electron emission related phenomena in materials under ultrashort pulsed laser irradiation of metals. *© 2010 American Institute of Physics.*
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The recent development of femtosecond laser systems resulted in a range of applications in different fields.[1–4] In spite of numerous efforts, the fundamental mechanisms of ultrashort laser ablation are still subject to discussion.[5–9] It has been demonstrated that electron emission can influence the processes occurring during ultrashort ablation.[10–12] For example, the concept of Coulomb explosion (CE) was suggested as a possible material removal mechanism during the gentle phase of ablation.[13] CE consists of electrostatic disintegration of several atomic layers as a result of positive surface charging due to electron emission. The possibility of CE has been theoretically studied for metals, semiconductors and dielectrics, assuming multiphoton photoemission (MPPE) and thermionic emission as mechanisms that induce charge separation in the target.[9] It was demonstrated that CE could act as a potential ablation mechanism in case of dielectrics but not in case of metals or semiconductors. Aside from CE, it has been suggested that laser induced electron emission from a metallic surface could cause breakdown in the ambient gas enclosing the target.[14]

When electrons are emitted from a solid, the negative space charge significantly influences the emission process.[15] Riffe *et al.*[16] investigated the space charge effect during thermionic emission from metals using a one-dimensional (1D) particle in cell (PIC) model. The study showed thermionic emission to be drastically reduced compared to the emission predicted by the commonly accepted Richardson–Duschmann equation. While in Ref. 9 it was demonstrated that using reasonably high fluences, MPPE would be dominant over thermionic emission for Au; MPPE was not considered in the PIC-simulations of Ref. 16. The space charge effect due to MPPE and thermionic emission can differ substantially, since the timescales of emission as well as the electron emission velocity distribution are quite different. Therefore, in this letter, thermionic emission as well as MPPE was implemented in the calculation of the space charge effect. While for semiconductors and dielectrics further investigation is necessary due to the different type of energy distribution of the emitted electrons, the results demonstrate that it is essential to take the space charge effect into account in theoretical studies concerning electron emission related phenomena in metals.

In the present letter, the space charge effect on electron emission from a copper surface is studied by means of a 1D collisionless PIC method.[17] The simulations were performed for a Gaussian pulse of 100 fs full width at half maximum and a wavelength of 800 nm, with an absorbed fluence of 450 J/m^2. The length of the PIC-grid was 500 nm, which corresponds to the assumed mean free path (MFP) of electrons in an N_2 atmosphere. The time- and spatial step were 1 fs and 1 Å, respectively.

The present PIC-method employs particle packages (macroparticles) with a certain weight, position and velocity representing the amount of emitted electrons.[17] The electron macroparticles are introduced at the surface boundary, and move according to their velocity and local electric field. When an electron reaches the remote boundary (i.e., 500 nm) it is considered to have escaped from the grid. When electrons are effectively emitted, the resulting positive charge of the system changes the boundary conditions for the electric field. Using Gauss' law for infinite plates, the following relation is given between the electric field at the remote boundary E_b and the effectively emitted charge area density Q_{lost}.

$$E_b = -\frac{Q_{lost}}{2\varepsilon}. \tag{1}$$

Q_{lost} is calculated as the sum of the effectively emitted charge per area at each timestep. Hence, the remote boundary condition is used for the implementation of the influence of the positive charge in the target. The Fowler–Dubridge theory provides the boundary condition at the target surface.[18] Here the total electron emission flux, J_{em}, is considered to be the sum of the thermionic emission flux and the total photoemission flux, respectively:

$$J_{em} = A_0 T_e^2 \left[\exp\left(\frac{\phi_w}{k_b T_e}\right) + \sum_{N=1}^{\infty} a_N F(X_N) \left(\frac{e}{h\nu}\right)^N I^N \right]. \tag{2}$$

The evaluation of the Fowler function, $F(X_N)$ with $X_N = (N \times h\nu - \phi_w)/k_b T_e$ is described in Ref. 19. Other variables are the Boltzmann constant k_b the Richardson–Duschmann constant A_0, the work function ϕ_w, the electron temperature T_e, the absorbed laser intensity I and a parameter a_N which is

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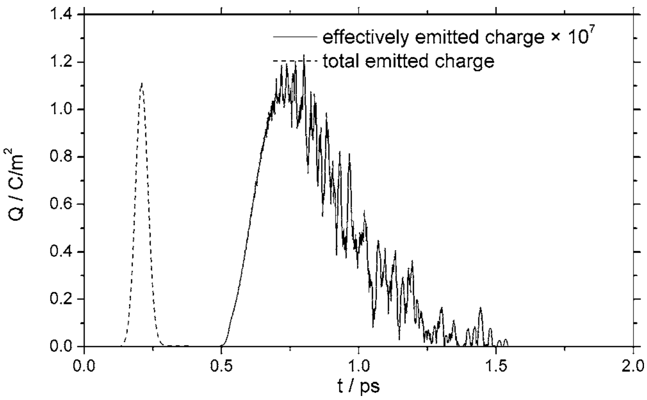

FIG. 1. Evolution of the total amount of charge emitted (dashed line) and the rescaled amount of effectively emitted charge (solid line) during each timestep.

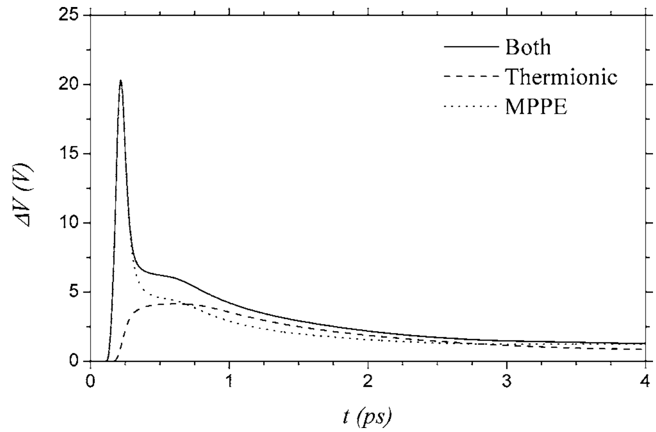

FIG. 2. The electrostatic potential barrier that electrons need to cross in order to reach the remote boundary of the PIC grid. The large and small dashed lines show results of only thermionic emission and 3PPE respectively, while the solid line represents the total effect.

proportional to the N-photon ionization coefficients. Under the applied conditions, the MPPE of Cu is dominated by three-photon photoelectron emission (3PPE).[9] The other terms in the MPPE term have been neglected. Since the Richardson–Duschmann equation assumes a Boltzmann distribution for the kinetic energies of the electrons in the conduction band, the velocities of the thermionic electrons at the surface are defined. For our calculations, we assume an initially Gaussian velocity distribution, using a standard deviation $\sqrt{\frac{2kT_e}{m_e}}$. The velocity at the maximum of the Gaussian was obtained from the following equation:

$$v_e = \sqrt{\frac{2(3h\nu - \phi_w)}{m_e}}. \tag{3}$$

The mean emission velocity is very low for the simulated conditions, since $3h\nu \approx \phi_w$ under the simulated conditions. The exact values of the material dependent properties a_3 and ϕ_w in the flux terms [see Eq. (2)] are not well known at extreme conditions occurring during fs-laser heating. ϕ_w and a_3 are set to 4.65 eV and $1\times10^{-46}(\mathrm{m}^2/\mathrm{A})^3$, respectively.[20] The T_e for Eq. (2) was calculated at the surface by means of a two temperature model,[5] adopting parameters from Refs. 21–23. We will present results for the first 10 ps of the simulation, since after 10 ps no more macroparticles were emitted.

As shown by the evolution of the emission process in Fig. 1, only electrons emitted in the early stage of the process can overcome the space charge potential due to the positive charge of the target and lower temperature at later times.

From Table I it is clear that the space charge effect caused by thermionic emission (as previously calculated by Riffe *et al.*[16]) differs substantially from the space charge effect caused by 3PPE. Despite their higher emission velocities, the electrons emitted by 3PPE do not increase the effective electron emission yield. On the contrary; because a larger amount of electrons is emitted in a shorter time span, the space charge potential quickly builds up to very large values. This reduces the ratio of effective to total electron emission for 3PPE compared to thermionic electrons by almost an order of magnitude (see Table I). The effect is also illustrated in Fig. 2.

TABLE I. Total amount of electrons emitted (Total) and amount of effectively emitted electrons (*E*sc), as well as the ratio of both, i.e., the relative yield. Results are shown for simulations including 3PPE and thermionic emission separately, and for a simulation including both electron emission processes.

	Total ($\mathrm{C/m^2}$)	*E*sc ($\mu\mathrm{C/m^2}$)	Ratio
Both	17.3	43.7	2.53×10^{-6}
Thermionic	1.60	26.5	1.65×10^{-5}
3PPE	15.7	43.5	2.77×10^{-6}

The potential barrier for calculations including 3PPE shows an intense peak at 200 fs, when the electron density above the surface reaches its maximum as shown in Fig. 2. This peak potential barrier decays in two regimes. At first, the decay originates only from electrons that return to the target. When the electrons escape at the remote boundary [see Fig. 1], the boundary conditions for the electric field change [see Eq. (1)], and the decay proceeds at a faster rate due to the net positive charge of the system.

When correlating the effectively emitted electrons and the absorbed laser fluence, a linear relation was found, as shown in Fig. 3. This is an interesting trend, since without considering the space charge, a third order polynomial is expected [see Eq. (2)]. Consequently the effect of the space charge created by 3PPE would be of second order. However, a quantitative treatment of this effect is complicated since all

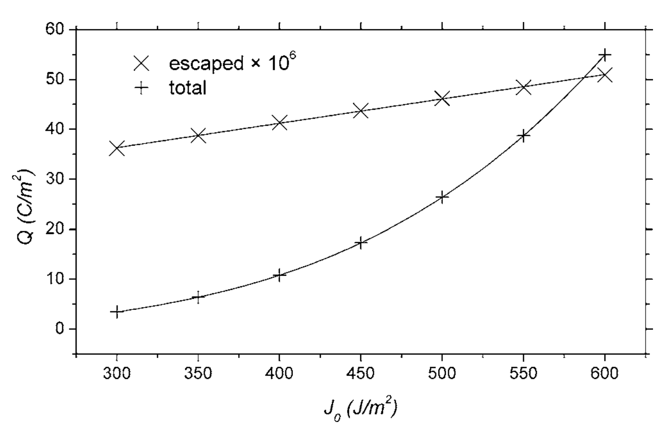

FIG. 3. Fluence dependence of the total amount of emitted electrons (left axis) and the amount of effectively emitted electrons (escaped; right axis).

electron macroparticles experience a different space charge potential at different timesteps and positions.

Finally note that there are some not well known properties in the calculations. So although the presented results show a clear trend, the model should not yet be used to make quantitative predictions. They do show a clear indication that the commonly accepted and applied theories significantly overestimate electron emission. More knowledge is needed about several fundamental aspects in order to make exact predictions. In order to study the applicability of the model, calculations were performed adopting a range of values for three less well known parameters; ϕ_w, a_3, and the MFP.

Variation in ϕ_w leads to two different effects. For a lower work function, more electrons will be emitted due to the smaller potential energy barrier for electron emission [see Eq. (2)], so the space charge effect will be more extreme, leading to a lower relative yield. On the other hand, the mean emission velocity is higher [see Eq. (3)], which means that due to increased kinetic energy the electrons can overcome a larger potential energy barrier. When varying ϕ_w from 3.6 to 5 eV, it was found that the amount of effectively emitted electrons is increased applying a lower value for ϕ_w (e.g., an increase of 20% for $\phi_w=3.6$ eV compared to $\phi_w=4.65$ eV). However the ratio of effectively emitted to the total amount of emitted electrons decreases (e.g., a factor 2 for $\phi_w=3.6$ eV compared to $\phi_w=4.65$ eV).

a_3 was taken as $1\times10^{-46}(\mathrm{m}^2/\mathrm{A})^3$ in the present study. When varied from 5×10^{-47} to $5\times10^{-46}(\mathrm{m}^2/\mathrm{A})^3$, it was demonstrated that this parameter does not have a major influence on the yield of effectively emitted electrons (44 to 42.9 $\mu\mathrm{C}/\mathrm{m}^2$, respectively). The total amount of emitted electrons is almost linearly proportional to a_3, so the ratio of effectively emitted to the total amount of emitted electrons goes down for higher values of a_3. A slightly decreased total yield was calculated applying higher values for a_3. This can be explained as follows. The space charge increases in a shorter time span and the mean emission velocity obtained from Eq. (3) is too small to overcome the space charge potential. Due to the large values for the space charge, the largest contribution is formed by the electrons emitted in the beginning of the emission process, as illustrated in Fig. 1. In this stage, the temperature is lower, which means that a smaller fraction of electrons have enough kinetic energy to overcome the space charge barrier when emission increases.

For 1D calculations, a threshold distance needs to be known to define when an electron is emitted, since otherwise no electrons would be effectively emitted. The assumption is made that electrons move over their MFP before they are effectively emitted when they collide with the ambient gas. The threshold distance is assumed to be the value of this MFP. This is another important parameter, since the amount of effectively emitted electrons is found to be roughly proportional to the inverse of the MFP.

The flux terms formulated by the Fowler–Dubridge theory as well as the electron emission velocity distributions are also based on assumptions concerning the electron distribution in the solid that might not be entirely applicable under the conditions considered for fs-laser ablation. Despite these assumptions, the general trend remains: the space charge reduces the effective electron emission by several orders of magnitude for any set of values for these parameters within a reasonable range. When adopting reasonable approximations, the PIC-method can provide a straightforward way to study several electron emission related processes.

In conclusion, a PIC-model was developed for the simulation of electron emission from a copper surface under fs-laser irradiation, considering the space charge potential created above the target. It is clear that, especially for MPPE, the space charge effect reduces the total yield of electrons to a very small fraction of the amount of originally emitted electrons. By varying the work function and the 3PPE ionization parameter it was demonstrated that the space charge substantially limits the electron emission. This demonstrates that theoretical studies of interesting electron emission related phenomena in metals should always take into account the space charge. Indeed, without an external voltage, the flux terms determined by the Fowler–Dubridge theory (or any other formulation neglecting the electrons outside the target) are of no reliable basis.

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