

Coupled Maxwell equations and semiclassical electronic and molecular dynamics simulation for analyzing laser ablation of silicon thin films

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A coupled simulation scheme combining Maxwell equations with semiclassical electronic and molecular dynamics based on the electron force field model has been developed to enable the description of interaction dynamics among electrons, ions in a condensed matter, and electromagnetic waves at a practical computational cost. This method is applied to investigate laser ablation of a silicon thin film induced by intense 100-fs pulsed laser irradiation. The simulation with normal incidence shows that a highly elevated electron temperature caused by light absorption leads to the initial ejection of electrons from a surface after the pulse has passed, facilitated by enhanced thermal fluctuations and a destabilized structure at the surface induced by energy relaxation. Subsequently, the positive net charges at the disordered surfaces, resulting from missing electrons, cause a Coulomb explosion of the surface ions accompanied by electrons. The explosive expansion of the vapor leads to the formation of small cavities and further inhomogeneous vapor-vacuum separation during the phase explosion process. Thus, the presented simulation provides a comprehensive microscopic understanding based on interaction dynamics among electrons, ions, and light within the semiclassical framework.

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I. INTRODUCTION

Laser ablation is a phenomenon in which constituents are explosively ejected in various forms such as electrons, plasma, ions, clusters, and fragments at the material surface caused by an intense laser pulse irradiation. Progress in high-power laser technology and declining equipment costs have made it easier to utilize laser ablation. Applications in engineering and industry, such as microfabrication of materials [1,2], synthesis of nanoparticles and thin films [2,3], and advancement of medical technology [4], are expected. The need for a fundamental understanding of light-matter interactions in the high-energy regime is therefore increasing. However, it remains difficult to obtain microscopic details about the complex and highly nonequilibrium processes of laser ablation from experimental measurements, while simulation studies using conventional methods yield only limited insights. Our present study aims (1) to develop a novel practical simulation method capable of describing high-energy light-matter interaction dynamics and (2) to elucidate the microscopic mechanisms of laser ablation using this method.

The primary players in laser ablation are light, electrons, and ions. In computational science, the first-principles methods are capable of accurately describing these interactions and time evolution. A representative method, time-dependent

density functional theory (TDDFT) [5,6], treats electron dynamics fully quantum mechanically under an external electric field [7–12] by solving the time-dependent Kohn-Sham equation and can also be combined with classical motion of ions [13]. An advanced approach has been developed to incorporate the propagation of an electromagnetic wave by coupling with Maxwell equations [14–18]. The coupling scheme with the classical electromagnetic wave has been reformulated for more efficient calculations [19,20]. Furthermore, the development of a coupled approach with photons or quantized electromagnetic fields, namely quantum-electrodynamical density functional theory, has been pursued for about a decade [21–23]. However, due to the considerable computational cost, it is difficult to handle temporal and spatial scales of laser ablation. Moreover, as is known, Ehrenfest molecular dynamics (MD) simulation, which would usually be suitable for systems with continuous electronic states (e.g., excited-state dynamics in solids), yields an unphysically higher electron temperature in the equilibrium state than ion temperature [24–26], which cannot describe proper energy relaxation from electrons to ions without artificial remedies [27]. This issue does not arise in a surface-hopping approach [24,28] which is usually applied to systems with discrete electronic states (e.g., molecular systems). The use of such an approach, however, is generally considered to have limited applicability to solid-state systems. A mixed quantum-classical model for solids thus requires careful consideration in addressing this issue.

To atomistically simulate the laser ablation, MD simulation based on a reactive force field allowing bond breaking and formation is commonly used [29–37]. This approach simulates ablation dynamics by adding initial kinetic energy, corresponding to the absorbed laser pulse energy, to atoms in the surface region. To take into account the effects of high

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electron temperature, this is extended to the two-temperature model, wherein background electron temperature is introduced in spatial blocks using a continuum model to exchange thermal energy with the atoms. Although the approach can simulate the ejection of atoms, dynamics of light and electrons cannot be described and their influences are introduced only in an *ad hoc* manner, as these are not explicitly treated in the calculation.

Aiming to enable a comprehensive description of the interaction dynamics among the three components, light, electrons and ions, while achieving computational efficiency, we previously extended a molecular simulation of the electron force field (eFF) model by introducing an external electric field as visible light [38,39], as a preliminary step. The eFF [40–48], which was originally developed by W. A. Goddard III and his collaborators, is a force-field-based explicit electron model in which electrons are treated as semiclassical particles with spherical Gaussian wave packets. It is capable of reproducing the ground-state structures of molecules and solids [41,47] and has also been successfully applied to systems in which plasma electrons emerge under extremely high temperature and pressure [40,43–45]. Therefore, our previously developed simulation can describe the dynamics of semiclassical electrons and classical ions under a spatially uniform external oscillating electric field, both in the ground-state and high-energy regimes. The particle-based model for both ions and electrons achieves low computational cost. It indeed successfully reproduced laser-induced melting of solid silicon by applying a pulsed field in femtosecond to picosecond range [39]. Here, in the present study, to enable a description of laser incidence on a material surface from the vacuum region, including optical aspects such as reflection, transmission and field enhancement, and suppression due to interference, we further extend the method by coupling with Maxwell equations to incorporate electromagnetic wave propagation.

By applying this extended method to an intense laser pulse incident on a material surface, this approach is expected to contribute to a deeper understanding of the underlying mechanisms of laser ablation than previously possible. A variety of mechanisms for laser ablation of dielectrics, semiconductors, and metals under various laser conditions have been reported based on experimental and computational studies. For example, field emission [49], multiphoton photoemission [50–52], and thermionic emission model [53,54] have been proposed for electron emission. For the ejection of ions and clusters, several mechanisms have been suggested, including Coulomb explosion model [55–59], electron pressure model [59–64], and plasma plume (or space charge) effects [65–67] due to charge separation in a broad sense. On a larger scale, shockwaves [68–71], and phase related mechanisms such as the phase explosion or explosive boiling model [69,72,73] associated with rapid melting and vaporization have been discussed for spallation, fragmentation, and bubble formation. In the mechanism at the initial stage, in particular, during or immediately after laser irradiation when the electrons and ions are ejected from the surface, the interaction dynamics among light and microscopic elementary components would play a crucial role. As mentioned above, however, conventional computational approaches such as the first-principles methods and

the two-temperature MD approach are difficult for describing these processes.

In this paper, we present and evaluate a novel computational method, Maxwell + eFF-MD simulation, that couples Maxwell equations for electromagnetic wave propagation with molecular dynamics based on the eFF model for semiclassical electrons and classical ions. As a first step in applying this method, we choose a silicon thin film as a relatively small and simple material. We first examine its linear optical response including thickness effects. We then investigate the ablation dynamics and its underlying mechanisms in a system where a 100-fs laser pulse, inducing one-photon excitation, is normally incident on a silicon thin film with a thickness of 14 nm. Since the force field used in this study is based on the original eFF model without fine tuning for this problem, and the electrons are treated semiclassically, the simulation results could be regarded, at this stage, as semiquantitative rather than quantitatively precise. Nevertheless, our developed method provides a microscopic yet comprehensive description of complex dynamical interplay among light, electrons, and ions as well as detailed insights on the laser ablation.

II. SIMULATION METHOD

A. Overview and setup

We consider a problem of irradiation of a pulsed laser onto the surface of a thin film of solid silicon, as illustrated in Fig. 1. The z axis is set to the propagation direction of the electromagnetic wave and the x and y axes are set perpendicular to the z axis with periodic boundary conditions. The electromagnetic wave is generated at the source plane in the vacuum region to the left of the thin film as shown in the figure. The wave, obtained by solving Maxwell equations, propagates along the z direction through the spatial grid points and interacts with the silicon thin film. The transmitted and reflected waves are absorbed at the absorption boundary planes at both ends of the z axis. Since the system is assumed to have much smaller cell lengths in the x and y directions than the wavelength and employs the periodic boundary conditions along them, scattered and radiated waves in the x and y directions may exhibit an undesired dependence on the cell lengths. To avoid this, such wave propagation is not considered in the present calculation. The electromagnetic wave is then treated as one dimensional, propagating only along the z axis. The silicon film is represented by the eFF model, consisting of ions treated as classical particles and electrons modeled as semiclassical particle-like wave packets. These are coupled with the electromagnetic wave through the equations of motion.

B. Electromagnetic wave

Time evolution of the electric and magnetic fields, $\vec{E}(z, t)$ and $\vec{B}(z, t)$, respectively, are described by Maxwell equations in Gaussian units,

$$\frac{\partial \vec{E}(z, t)}{\partial t} = c \nabla \times \vec{B}(z, t) - 4\pi \vec{J}(z, t), \quad (1)$$

$$\frac{\partial \vec{B}(z, t)}{\partial t} = -c \nabla \times \vec{E}(z, t), \quad (2)$$

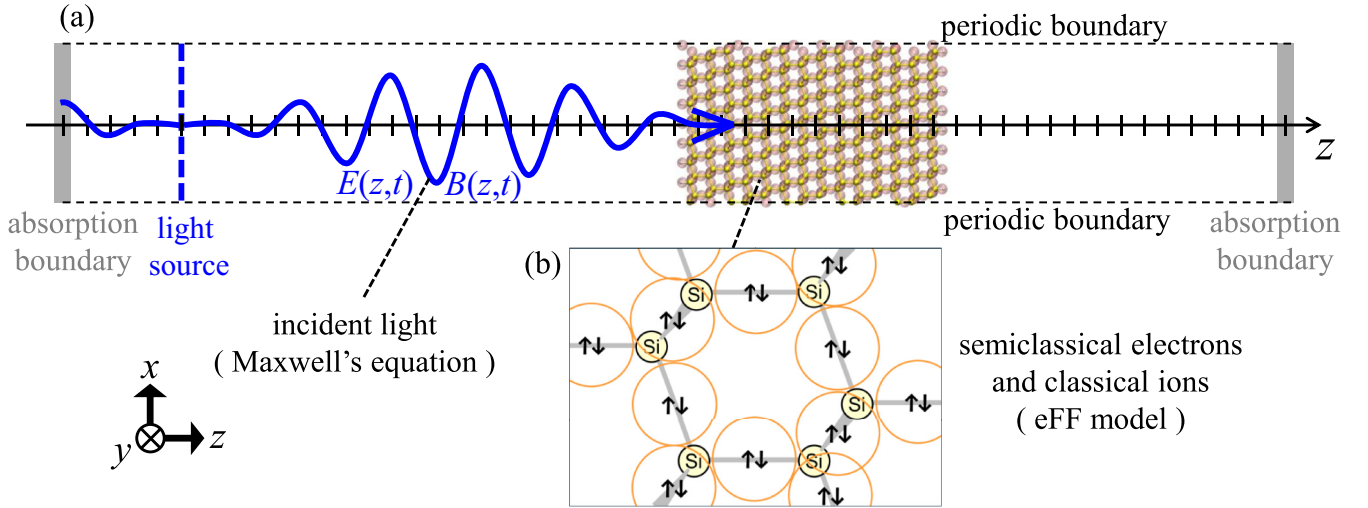


FIG. 1. (a) Schematic illustration of simulation setup. (b) Positions of ions (shown as smaller circles labeled “Si”) and valence electrons (shown as larger circles with up- and down-spin arrows) in the silicon crystal treated in the eFF model. A pair of the up- and down-spin electrons, located at the same position in the illustration, is placed between two adjacent ions forming a bonding state. Solid gray lines are drawn for convenience.

where c is the speed of light and $\vec{J}$ denotes the electric current density. The magnetic current density is not included here, as the magnetic polarization of a material is ignored. Since we do not consider the propagation in the x and y directions as stated above, the z components of $\vec{E}$ and $\vec{B}$ are not solved (i.e., only the x and y components are solved and the z components are forced to zero). To express the fields, the spatial grid points, $\{z_k\}$, on the z coordinate are introduced. The electric and magnetic fields at the grid point z_k are denoted by $\vec{E}_k(t)$ and $\vec{B}_k(t)$, respectively, instead of $\vec{E}(z_k, t)$ and $\vec{B}(z_k, t)$. Maxwell equations for them are rephrased as

$$\frac{\partial \vec{E}_k(t)}{\partial t} = c \nabla \times \vec{B}_k(t) - 4\pi \vec{J}_k(t), \quad (3)$$

$$\frac{\partial \vec{B}_k(t)}{\partial t} = -c \nabla \times \vec{E}_k(t). \quad (4)$$

Here $\vec{J}_k$, the electric current density at z_k , serves as the interaction from a material. Note that a macroscopic parameter such as the dielectric constant is not necessary in the equations because the current density, which is directly determined by the ions and electrons described by the eFF model, plays this role. The polarization is naturally included in this interaction through the explicit electronic and ionic response to the field.

C. Ions and electrons

Ions and valence electrons of the silicon film are represented by the eFF model. Core electrons are implicitly included in an ion through an effective potential. Si atom then consists of four valence electrons and a $4+$ charged core-nucleus bound ion. A covalent bond in the eFF model is formed as a structure in which the up- and down-spin electrons are located between neighboring Si atoms as illustrated in Fig. 1(b). The field-matter interaction has been incorporated in our previous study [39]. The extended model is used previously for a system under an external field, whereas in the present work it is coupled with Maxwell equation in Eq. (3).

1. Equations of motion

A semiclassical valence electron is described as a spherical Gaussian wave packet. The wave function of the electrons as functions of electron coordinates $\{\vec{r}_j\}$ and time t is given in the form of the Hartree product approximation by

$$\Psi(\{\vec{r}_j\}, t) \propto \prod_j^{\text{ele}} \exp \left[- \left(\frac{1}{s_j^2} - \frac{2p_{s_j}}{s_j} \frac{i}{\hbar} \right) |\vec{r}_j - \vec{x}_j|^2 + \frac{i}{\hbar} \vec{p}_{x_j} \cdot \vec{r}_j \right], \quad (5)$$

where center position $\vec{x}_j(t)$ and size $s_j(t)$ of the Gaussian wave packet are dynamical variables of the j th electron, and $\vec{p}_{x_j}(t)$ and $p_{s_j}(t)$ are its conjugate translational and radial momenta, respectively.

Taking the expectation values by integrating over $\vec{r}_i$ with Eq. (5), the Ehrenfest theorem leads to Newtonian-like equations of motion for the variables of $\{\vec{x}_j\}$, $\{s_j\}$, $\{\vec{p}_{x_j}\}$, and $\{p_{s_j}\}$. To treat light-matter interaction, the Newtonian-like equations of motion of the original eFF model [40] was extended previously [39] by (i) adding Coulomb force term between electron/ion charge and external electric field and (ii) introducing effective electron masses that is adjustable depending on the bonding states. In this study, the external electric field employed in (i) is replaced by the electromagnetic wave. Lorentz force is also added. Denoting the electric and magnetic fields of the electromagnetic wave at the electron position $\vec{x}_i$ as $\vec{E}_i = \vec{E}(\vec{x}_i, t)$ and $\vec{B}_i = \vec{B}(\vec{x}_i, t)$, respectively, the Newtonian-like equations in the present simulation are written by

$$\vec{p}_{x_i} = m_{x_i}^* \frac{d\vec{x}_i}{dt} (= m_{x_i}^* \vec{v}_i), \quad (6)$$

$$\frac{d\vec{p}_{x_i}}{dt} = - \frac{\partial U_{\text{tot}}}{\partial \vec{x}_i} + e(\vec{E}_i + \vec{v}_i/c \times \vec{B}_i), \quad (7)$$

$$p_{s_i} = m_{s_i}^* \frac{ds_i}{dt}, \quad (8)$$

$$\frac{dp_{s_i}}{dt} = -\frac{\partial U_{\text{tot}}}{\partial s_i}, \quad (9)$$

where $e(= -1)$ is the electron charge and U_{tot} is the total potential energy function for ions and electrons. $\vec{v}_i$ defined by $\frac{d\vec{x}_i}{dt}$ is the velocity of the i th electron. The effective electron mass for $\vec{x}_i$, $m_{x_i}^*$, and that for s_i , $m_{s_i}^*$, in extension (ii) are introduced to better reproduce the absorption wavelength. In the original form [40], the inertial electron masses are written by $m_{x_i}^* = m_e$ and $m_{s_i}^* = (3/4)m_e$ [where $m_e(= 1 \text{ a.u.})$ is the electron mass], respectively. The dynamical adjustments of $m_{x_i}^*$ and $m_{s_i}^*$ are explained later. We note that the effects of tunneling and zero-point energy are included through $s_i(t)$ in the semiclassical framework [74].

On the other hand, an ion follows Newtonian equation of motion that is extended by adding the Coulomb and Lorentz forces from the electromagnetic field,

$$\vec{P}_a = M_a \frac{d\vec{R}_a}{dt} (= M_a^* \vec{V}_a), \quad (10)$$

$$\frac{d\vec{P}_a}{dt} = -\frac{\partial U_{\text{tot}}}{\partial \vec{R}_a} + Z_a(\vec{E}_a + \vec{V}_a/c \times \vec{B}_a), \quad (11)$$

where $\vec{R}_a$, $\vec{V}_a$, and $\vec{P}_a$ denote the position, velocity, and momentum of the a th ion, respectively, and M_a and Z_a are the ionic mass and charge. $\vec{E}_a$ and $\vec{B}_a$ denote $\vec{E}(\vec{R}_a, t)$ and $\vec{B}(\vec{R}_a, t)$, respectively.

U_{tot} consists of electrostatic interaction term between the ions, $U^{\text{ion-ion}}$, that between the electrons, $U^{\text{ele-ele}}$, that between the ions and electrons, $U^{\text{ion-ele}}$, quantum electronic kinetic term due to Heisenberg uncertainty relationship, U_s^{ele} , and Pauli interaction term, U_{Pauli} , that is,

$$U_{\text{tot}} = U^{\text{ion-ion}} + U^{\text{ion-ele}} + U^{\text{ele-ele}} + U_s^{\text{ele}} + U_{\text{Pauli}}. \quad (12)$$

U_{Pauli} is effectively given to compensate for shortcoming of the Hartree product form of Eq. (5).

The constituent energy terms in U_{tot} are as follows: The ion-ion, electron-electron, and ion-electron electrostatic interaction terms are given respectively by

$$U^{\text{ion-ion}} = \sum_{a>b}^{\text{ion}} \frac{Z_a Z_b}{r_{ab}} \text{erf} \left(\frac{\sqrt{2} r_{ab}}{\sqrt{s_{\text{core},a}^2 + s_{\text{core},b}^2}} \right), \quad (13)$$

$$U^{\text{ele-ele}} = \sum_{i>j}^{\text{ele}} \frac{e^2}{r_{ij}} \text{erf} \left(\frac{\sqrt{2} r_{ij}}{\sqrt{s_i^2 + s_j^2}} \right), \quad (14)$$

$$U^{\text{ion-ele}} = \sum_a^{\text{ion}} \sum_i^{\text{ele}} \frac{Z_a e}{r_{ai}} \text{erf} \left(\frac{\sqrt{2} r_{ai}}{\sqrt{s_{\text{core},a}^2 + s_i^2}} \right), \quad (15)$$

where the indices of a and b indicate the a th and b th ions, respectively, while the indices of i and j indicate the i th and j th electrons. r_{ab} , r_{ai} , and r_{ij} represent the distances between two particles with the corresponding indices. $Z_a(Z_b)$ is the ionic charge. $s_{\text{core},a}$ denotes a fixed parameter of particle radius of

the core electrons for the a th ion, where $s_{\text{core},a} = 0$ for the ion (nucleus) without the core electrons. The quantum electronic kinetic term is given by

$$U_s^{\text{ele}} = \frac{\hbar^2}{m_e} \sum_i^{\text{ele}} \frac{3}{2s_i^2}. \quad (16)$$

The Pauli potential term consists of the same spin ($\sigma_i = \sigma_j$) interaction, $E_{ij}^{\uparrow\uparrow}$, and the opposite ($\sigma_i \neq \sigma_j$) one, $E_{ij}^{\uparrow\downarrow}$, for between valence-valence electrons, and the core-valence electrons interaction, $E_{ij}^{\text{core-ele}}$, that is,

$$U_{\text{Pauli}} = \sum_{i>j}^{\text{ele}(\sigma_i=\sigma_j)} E_{ij}^{\uparrow\uparrow} + \sum_{i>j}^{\text{ele}(\sigma_i \neq \sigma_j)} E_{ij}^{\uparrow\downarrow} + \sum_a^{\text{ion(core)}} \sum_i^{\text{ele}} E_{ai}^{\text{core-ele}}. \quad (17)$$

These terms are expressed by

$$E_{ij}^{\uparrow\uparrow} = \left(\frac{S_{ij}^2}{1 - S_{ij}^2} + (1 - \rho) \frac{S_{ij}^2}{1 + S_{ij}^2} \right) \Delta T_{ij}, \quad (18)$$

$$E_{ij}^{\uparrow\downarrow} = -\frac{\rho S_{ij}^2}{1 + S_{ij}^2} \Delta T_{ij}, \quad (19)$$

$$(\rho = -0.2),$$

where

$$S_{ij} = \left(\frac{2}{\bar{s}_i/\bar{s}_j + \bar{s}_j/\bar{s}_i} \right)^{3/2} \exp \left(-\frac{\bar{r}_{ij}^2}{\bar{s}_i^2 + \bar{s}_j^2} \right), \quad (20)$$

$$\Delta T_{ij} = \frac{\hbar^2}{m_e} \left[\frac{3}{2} \left(\frac{1}{\bar{s}_i^2} + \frac{1}{\bar{s}_j^2} \right) - \frac{2(3(\bar{s}_i^2 + \bar{s}_j^2) - 2\bar{r}_{ij}^2)}{(\bar{s}_i^2 + \bar{s}_j^2)^2} \right], \quad (21)$$

$$(\bar{s}_i = 0.9 \times s_i, \quad \bar{r}_{ij} = 1.125 \times r_{ij}),$$

and

$$E_{ai}^{\text{core-ele}} = A_a \exp \left(-\frac{B_a r_{ai}^2}{C_a + s_i^2} \right). \quad (22)$$

The functional form and parameters A_a , B_a , and C_a in Eq. (22) are for Si atomic species.

2. Effective electron mass parameter

To adjust the absorption wavelength, the inertial electron masses for x_i and s_i are replaced by the effective mass parameters, $m_{x_i}^*$ and $m_{s_i}^*$, as shown in Eqs. (6) and (8). To better reproduce the optical response for both bound (or bonding) and unbound electronic states, i.e., corresponding to the solid and liquid or gas phases respectively, further extension of the parameters is introduced [39]. The effective masses for the i th electron are then expressed by using the scaling factors α_{x_i} and α_{s_i} as

$$m_{x_i}^* = \alpha_{x_i}(\eta_i) m_e, \quad (23)$$

$$m_{s_i}^* = \alpha_{s_i}(\eta_i) \left(\frac{3m_e}{4} \right). \quad (24)$$

Both α_{x_i} and α_{s_i} are functions of an order parameter η_i that reflects the bound (or unbound) electronic state. Denoting

them collectively as α_{x_i, s_i} , it is given by

$$\alpha_{x_i, s_i}(\eta_i) = \frac{\alpha_{x, s}^{\text{bd}} - \alpha_{x, s}^{\text{ubd}}}{2} \text{erfc}\left(\frac{\eta_i - \eta_c}{\Delta\eta_c}\right) + \alpha_{x, s}^{\text{ubd}}, \quad (25)$$

where the factor smoothly varies from $\alpha_{x, s}^{\text{bd}}$ in the smaller η_i region (the bound (or solid) state) to $\alpha_{x, s}^{\text{ubd}}$ in the larger η_i region (the unbound (or liquid or gas) state) with width of about $\Delta\eta_c$ across $\eta_i = \eta_c$. To maintain energy conservation, the velocities are adjusted at every time step compensating for the energy change due to the variation in the scaling factors by multiplying the velocities by $\sqrt{\alpha_{x_i, s_i}(t)/\alpha_{x_i, s_i}(t + \Delta t)}$, where Δt is the time step width.

The order parameter η_i is defined based on the deviation of the i th electron from its optimal position between the nearest two ions denoted as $\Delta l_i(t)$. In the crystalline structure, the optimal position of the valence electron forming a Si-Si bond is the midpoint between the two ions. At room temperature, the valence electron stays around the optimal position, which might be considered “bonding position” (corresponding to a small Δl_i), while at high temperature the electron can leave this region and behave as an unbound electron in the molten or vaporized state (corresponding to a larger Δl_i). During the simulation, to avoid use of instantaneous values of Δl_i that are excessively large or small, the time-averaged Δl_i over a short time block of $\Delta t^{(\Delta l)}$, $\overline{\Delta l_i}$, is calculated every $\Delta t^{(\Delta l)}$ interval. η_i used in Eq. (25) is employed as linearly interpolated value between the latest and the second latest $\overline{\Delta l_i}$, albeit a crude estimate.

D. Interaction between electromagnetic field and ions/electrons

Interaction between electromagnetic field and ions/electrons occurs through the electric current density $\vec{J}_k$ in Maxwell equation of Eq. (3) and the Coulomb and Lorentz force terms in the equations of motion of Eqs. (7) and (11).

In Eq. (3), $\vec{J}_k$ at z_k is defined by the motion of the electrons and ions in the grid cell of the index k as

$$\vec{J}_k = \frac{1}{\Delta V} \left[\sum_i^{\text{ele(at } k)} e \vec{v}_i + \sum_a^{\text{ion(at } k)} Z_a \vec{V}_a \right]. \quad (26)$$

ΔV denotes the grid cell volume defined by $L_x L_y \Delta z$, where L_x and L_y denote the lengths of the unit cell along the x and y directions, respectively, and Δz denotes the grid cell size along the z direction. The summations are taken over the electrons and ions at the grid point z_k . If the summations are taken over the particles simply within the grid cell, then $\vec{J}_k(t)$ changes abruptly when particles move in or out. To avoid it, we employ a first-order linear weighting technique in the z direction, where the current vector of each electron and ion is linearly distributed to the two nearest grid points. This is known as the “clouds-in-cell method” [75] often used in particle-in-cell simulation in plasma physics.

In Eqs. (7) and (11), $\vec{E}_i$ (or $\vec{E}_a$) is obtained by linearly interpolating the electric field values $\{\vec{E}_k\}$ of the electromagnetic wave at the two nearest grid points along the z direction. $\vec{B}_i$ (or $\vec{B}_a$) is also obtained in the same way.

E. Total energy

The total energy of the unit cell is given by the sum of the energies of the electrons and ions and electromagnetic field inside the cell, E_{mat} and $E_{\text{em}}^{\text{uc}}$, respectively, as

$$E_{\text{tot}}^{\text{uc}} = E_{\text{em}}^{\text{uc}} + E_{\text{mat}}. \quad (27)$$

The electromagnetic field energy inside the unit cell is written by

$$E_{\text{em}}^{\text{uc}} = \frac{\Delta V}{8\pi} \sum_k^{z\text{-grid}} (|\vec{E}_k|^2 + |\vec{B}_k|^2). \quad (28)$$

The total energy of the electron-ion system is written by

$$E_{\text{mat}} = K^{\text{ion}} + K^{\text{ele}} + U_{\text{tot}}, \quad (29)$$

where kinetic energy terms of the ions and electrons are, respectively,

$$K^{\text{ion}} = \sum_a^{\text{ion}} \frac{|\vec{P}_a|^2}{2M_a} \quad (30)$$

$$K^{\text{ele}} = \sum_i^{\text{ele}} \left(\frac{|\vec{p}_{x_i}|^2}{2m_{x_i}^*} + \frac{p_{s_i}^2}{2m_{s_i}^*} \right). \quad (31)$$

Since the simulation uses the absorption boundary condition, $E_{\text{tot}}^{\text{uc}}$ does not conserve. As it is convenient to confirm the energy conservation, the energy of the electromagnetic field outside the unit cell in the z direction, $E_{\text{em}}^{\text{out}}$, that is, the field energy absorbed by the boundary conditions at the ends of the z axis and the incident field energy before entering the system at the source position, can be added. Then, the total energy defined by

$$E_{\text{tot}} = E_{\text{em}} + E_{\text{mat}}, \quad (32)$$

where

$$E_{\text{em}} = E_{\text{em}}^{\text{uc}} + E_{\text{em}}^{\text{out}}, \quad (33)$$

is conserved. The added term is given by

$$E_{\text{em}}^{\text{out}}(t) = E_{\text{inc}}^{\text{out}}(t) + \left(\int_0^t S_z(z_R, t') dt' - \int_0^t S_z(z_L, t') dt' \right) \times L_x L_y, \quad (34)$$

where $E_{\text{inc}}^{\text{out}}$ is the field energy that does not yet enter (that is, sum of $E_{\text{inc}}^{\text{out}}$ and the field energy that entered the system is equal to the total incident wave energy). The energies of the absorbed field at the left and right boundary conditions are written by the time integral of the energy flow up to time t at the grid points adjacent to the left and right ends (denoted by z_L and z_R , respectively), given by the z component of Poynting's vector $S_z(z_{R/L}, t')$.

F. Computational details

1. Systems, parameters, and equilibration

The silicon thin films with thicknesses of about 1.8, 4.6, 14.0, and 23.5 nm in the z direction are used. Initial structures of the thin films are prepared by placing crystalline silicon in a cell that is long along the z axis with side lengths of 2.660 and 2.304 nm in the x and y directions, respectively, where periodic boundary conditions are applied in the x and

y directions. Each Si atom on Si(111) surfaces facing the z direction is capped by a terminating atom forming a single bond. The terminating atom here is chosen to be an artificial species that consists of a +1 charged nucleus and an electron with the same mass as the Si atom in order to suppress the influences arising from the choice of terminating species. We refer to the terminating atom as $\text{Si}^{(\text{cap})}$ hereafter. Then the thin films contain 480, 1344, 4224, and 7104 Si atoms in order of increasing thickness, along with 96 terminating atoms for all thicknesses. Two valence electrons of opposite spins are placed for each bond at the midpoint between two adjacent ions as a bonding state. Since each Si atom consists of a +4 charged ions and two up-spin and two down-spin valence electrons, the number of valence electrons in the system of, for example, the 14-nm-thick film is 16992, which gives a total of 21312 particles including the ions.

The original parameters of the eFF model given in Ref. [47] are used for the electron-ion system. The long-range interaction is cutoff using a taper function that smoothly decays to zero at a distance of 10.85 Å. For the scaling factors of the effective electron masses, $\alpha_x^{\text{bd}} = 3.8$ and $\alpha_s^{\text{bd}} = 95.0$ for the bonding state are used, while α_x^{ubd} and α_s^{ubd} are chosen to 1 (i.e., no scaling) for the unbound state, as determined in our previous study [39]. η_c , $\Delta\eta_c$, and $\Delta t^{(\Delta I)}$ are chosen to be 0.55 Å, 0.07 Å, and 5 fs, respectively.

The spatial grid points along the z axis, where Yee's grid system [76] is employed, are set with a spacing $\Delta z = 0.2715$ nm. One-dimensional Mur's absorption boundary conditions [76] are applied to the electric and magnetic field at both ends of the z axis.

To prepare equilibrium state at room temperature, simulation is carried out for several tens of picoseconds after geometry optimization of the initial configuration. During the equilibrating process, temperature is controlled by velocity scaling method every 100 fs for the ions and every 10 fs for the electrons, where the electron temperature is defined as $\frac{K^{\text{ele}}}{2k_B N^{\text{ele}}}$ (k_B and N^{ele} denote Boltzmann constant and the number of electrons, respectively). The center of mass of the thin film is fixed. The electromagnetic field is not yet included. The equations of motion for electrons and ions are integrated by leapfrog scheme with 0.01 fs. In the present study, the temperature is set to 700 K as the effective room temperature (hereafter referred to as effective 300 K), based on the calculation of the temperature factor using the force-field in the previous work [39].

After reaching the thermal equilibrium of the electron/ion system, the equations of motion for the electric and magnetic fields are introduced to obtain the equilibrium state including the field, and the coupled simulation is carried out for 100 fs using multiple time steps of 0.002 fs for the electrons/ions and 0.0005 fs for the field without the temperature control and the constraint of the center of mass.

The laser electromagnetic wave is then incident from the left vacuum region. Two types of light-irradiation simulations are performed: a linear response simulation using weak impulsive field to evaluate optical spectra (reflection, transmission, and absorption) and a laser-ablation simulation using a strong pulsed field.

2. Linear response simulation

In the linear response simulation, weak impulsive field is generated at $z = -10$ nm by giving a spatial Gaussian electric field with 1 nm width along z only at the first step as a step function in time, where the left surface of the thin film is around $z = 0$ nm. To evaluate the optical spectra, the Fourier transforms of the fields detected at the positions $z^{(L)} = -15$ nm (left) and $z^{(R)} = 15$ –28 nm (depending on the film thickness) (right) in the vacuum regions, denoted as $\vec{E}^{(L)}(\omega)$ and $\vec{E}^{(R)}(\omega)$, respectively, are calculated. Using the reference fields $\vec{E}_0^{(L)}(\omega)$ and $\vec{E}_0^{(R)}(\omega)$ separately calculated from a field-only simulation in vacuum (i.e., without the thin film), the transmittance, reflectivity, and absorptivity are calculated respectively by

$$T(\omega) = |\vec{E}^{(R)}(\omega)|^2 / |\vec{E}_0^{(R)}(\omega)|^2,$$

$$R(\omega) = |\vec{E}^{(L)}(\omega) - \vec{E}_0^{(L)}(\omega)|^2 / |\vec{E}_0^{(L)}(\omega)|^2,$$

$$A(\omega) = 1 - T(\omega) - R(\omega).$$

3. Laser-ablation simulation

In the laser-ablation simulation, we focus on the thin film with a thickness of 14 nm, where a longer cell ranging from about -60 nm to 75 nm along the z direction is used to describe ejected electrons and ions. To prevent radial expansion of electron beyond the cutoff distance in vacuum region, a harmonic restraint is imposed on $s_i(t)$ above 10 Å. The strong pulsed electric field polarized in the x direction is generated by using oscillating electric current density at $z = -40$ nm, according to the soft source method [77]. The generated incident wave has a squared-cosine envelope with the full width at half maximum duration of 100 fs (corresponding to total duration of 274.5 fs). The field frequency is set to 3.0 eV to induce one-photon absorption (linear excitation), and the electric field intensities at maxima are chosen as 7.0×10^{11} and 1.2×10^{12} W/cm², corresponding to fluences of 0.07 and 0.12 J/cm², respectively. Since two-photon absorption is underestimated in the eFF model without adjustments or corrections, it is effectively not included in the calculation. As the one-photon absorption is dominant, we regard two-photon absorption as negligible.

4. Analyses

In analyzing the driving force for ion ejection, as shown in the Sec. III C 5, we consider the forces on an ion with bound electrons, i.e., an ion-electron complex in the simulation, to account for its charge state. The detailed definition is provided in Sec. E in the Supplemental Material [78]. The forces in the eFF model can be decomposed into the Coulomb force and repulsive forces arising from the Pauli potential and the effective core potential. To clarify the ejection mechanism at the rear surface, we further decompose these forces into the components from particles located on the left (inner) side and from those located on the right (outer) side. That is, the decomposed force components acting on the ion (or ion-electron complex) are Coulomb force from an ion on the left and right sides, $F_{L/\text{cl}}^{\text{ion}}$ and $F_{R/\text{cl}}^{\text{ion}}$, Coulomb force from an electron on the left and right sides, $F_{L/\text{cl}}^{\text{ele}}$ and $F_{R/\text{cl}}^{\text{ele}}$, and the repulsive forces arising from

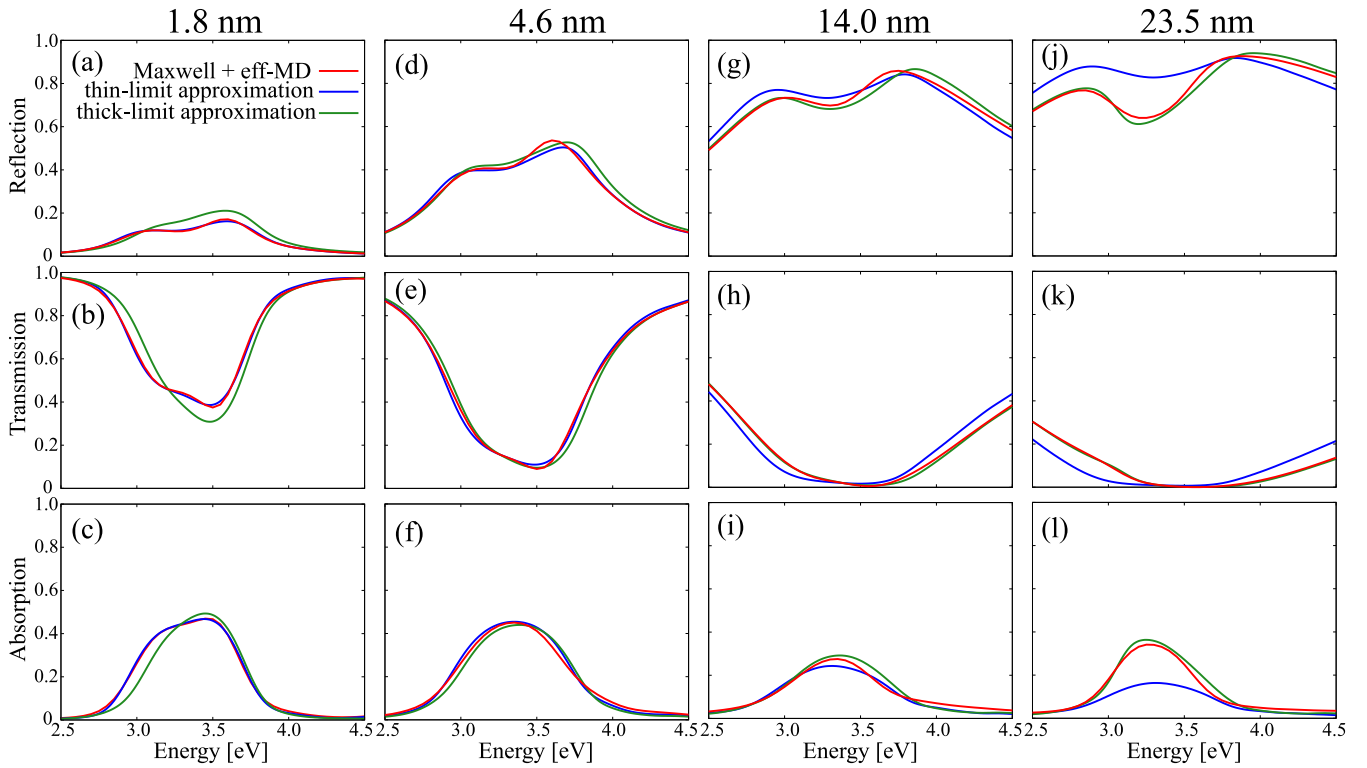


FIG. 2. Reflection, transmission, and absorption spectra calculated using the Maxwell + eFF-MD simulation (red lines) as well as semianalytical thin-limit (blue lines) and thick-limit (green lines) approximation models for a silicon film with a thickness of 1.8 nm [(a), (b), and (c)], 4.6 nm [(d), (e), and (f)], 14.0 nm [(g), (h), and (i)], and 23.5 nm [(j), (k), and (l)] at effective 300 K. Each spectrum is obtained by averaging over five samples.

the Pauli and effective core potentials from the left and right sides, $F_{L/\text{rep}}$ and $F_{R/\text{rep}}$, where the repulsive force from the Pauli potential represents electron-repulsive interaction acting on the bound electron in the ion-electron complex, and the repulsive force from the effective core potential represents the interaction between valence-core electrons. The internal force within the complex is not included in the decomposed force components.

Analysis plots of distribution along the z axis shown later are all averaged over a time block of 100 fs and over electrons and ions located within a spatial window of 3 Å in the z coordinate. The computational details for analyses are provided in the results section or Sec. E of the Supplemental Material [78].

5. Computational cost

Computation of the laser-ablation simulation shown in Sec. III C (the silicon film with a thickness of 14 nm) is completed in 14.6 h per 1 ps using a single node (48 cores) without fine tuning. On the other hand, a TDDFT-Maxwell simulation of a similar system size can be performed if very large computational resources and highly tuned code are used. Benchmarks of the SALMON code have shown a computational cost of about 1 s/step for 10 000 atom system using 27 648 computer nodes [17], which is hardly practical. Compared with an ordinary MD simulation using a force-field model, the computational cost of the present method is higher because time step must be much smaller to treat high-energy

electron dynamics. Nevertheless, the method is still quite practical and even larger systems could be treated using parallel computing.

III. RESULTS AND DISCUSSION

A. Linear-response: Reflectance, transmittance, and absorbance

We first show, in Fig. 2, $R(\omega)$, $T(\omega)$, and $A(\omega)$ of a silicon thin film with a thickness of 1.8, 4.6, 14.0, and 23.5 nm at the effective 300 K, obtained from the linear-response calculations. The results obtained by the Maxwell + eFF-MD simulation are shown as the red lines. The absorption peaks appear around 3.2–3.5 eV depending on the thickness. These peak positions are near that of bulk solid silicon calculated in the previous study [39]. Since the eFF model is based on the semiclassical approximation, the calculation cannot reproduce the shape of the spectrum accurately, but it captures the main peak reasonably well.

The spectra of the thin films include effects of the surfaces and multiple reflections. To clarify these effects, following the approaches used in Ref. [15], we also plot two semianalytical spectra calculated using two different extremes in each panel of Fig. 2. One is the spectrum that includes the surface effect but not multiple reflections, shown as the blue line labeled “thin-limit approximation.” In this calculation, the same film structure as the Maxwell + eFF-MD model is used whereas zero-thickness limit is applied to Maxwell equations. The other is the spectrum that includes the multiple reflections

but not the surface effect, shown as the green line labeled “thick-limit approximation.” This is calculated using a unit cell of the bulk solid silicon without the surfaces.

The figures in the thinnest case of 1.8 nm show that all R , T , and A spectra obtained by the Maxwell + eFF-MD simulation almost coincide with those of the thin-limit approximation, while they do not match the thick-limit approximation. For a thickness of 4.6 nm, the spectra lie between the two approximations but are closer to the thin limit. The spectra for the thicker case of 14 nm still lie between the two but shift toward the thick limit. In the case of the thickness of 23.5 nm, the spectra obtained from the Maxwell + eFF-MD simulation are very close to those from the thick-limit approximation, whereas the spectra obtained from the thin-limit approximation quite differ. This indicates that a thickness of 23.5 nm is sufficient for the slab to exhibit the bulklike feature with negligible surface effect, and the thin-limit approximation without the multiple reflections cannot adequately describe the optical feature at this thickness. Thus, the present simulation successfully shows that, with increasing film thickness, R , T , and A spectra shift from the thin limit that includes the surface effect toward the thick limit that is described by the bulklike property with multiple reflection effect. The same trend has been shown by the first-principles study [15].

B. Laser irradiation below damage threshold

We next show the simulation results of laser irradiation using a 100-fs pulse with a photon energy of 3.0 eV on a silicon film 14 nm thick at effective 300 K. Fluences of 0.07 J/cm² (below damage threshold in our calculation) and 0.12 J/cm² (above the threshold) are chosen, where the estimated threshold in the present calculation, defined as a lower limit that prevents electron ejection, is 0.08–0.09 J/cm². The results for the lower fluence of 0.07 J/cm² are shown here below.

Upon laser irradiation, energy conservation can be confirmed in the present simulation, where the electromagnetic field energy is deposited in the thin film during the interaction, with the sum of the light and material energies being constant (see Sec. A of the Supplemental Material (Fig. S1) [78]).

To see where the film absorbs and how the energy flows, temperature distributions of electrons and ions along the z axis at selected times are shown in Fig. 3. Before irradiation, the electrons and ions are both in the equilibrium state at 700 K (effective 300 K). After the onset of irradiation, the electron temperature rapidly increases by photoexcitation. At 0.2 ps, when the pulse has passed its peak intensity but is still propagating through the film, it reaches as high as 2200 K near the rear surface while remaining as low as 1300 K near the front surface. This nonuniform electron temperature rise is attributed to the constructive interference of the multiple reflection waves at the rear surface [79] in this setup. After the pulse has passed, the electron temperature becomes a spatially uniform reaching a quasiequilibrium state, which is almost achieved by 0.7 ps. On the other hand, the rise in the ion temperature is much smaller. According to our previous study [39], the melting point of bulk silicon estimated using the eFF model is 2550 K. The silicon film, therefore, would remain in the solid state with this temperature. Although the

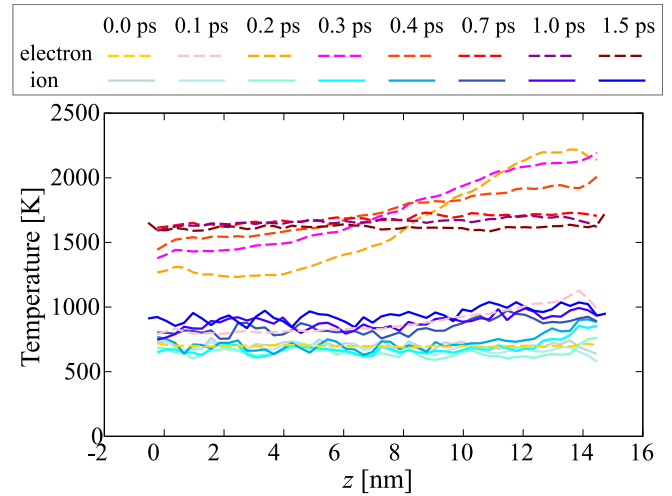


FIG. 3. Temperature distributions of electrons and ions along the z axis at selected times during and after laser irradiation with a fluence of 0.07 J/cm².

energy relaxation from electrons to ions does not significantly occur in this time interval, small increase has begun at the rear surface at 0.3 ps due to the relaxation from the higher-energy electrons. Overall ion temperature rises a little after 0.7 ps.

To confirm the microscopic state of the silicon film, we evaluated the changes in the spatial distributions of the order parameter $\langle \Delta l(z, t) \rangle$ for electrons, the root-mean-square deviation (RMSD) of the ionic positions, and the number densities of ions and electrons. The plots are shown in Figs. S2 and S3 together with the detailed explanation in Sec. B of Supplemental Material [78]. In brief, during the relaxation process shown in Fig. 3, electrons remain near the optimal bonding positions across the entire region with the order parameter staying below 0.2 Å. The ions also remain near the atomic positions in the crystal structure exhibiting small RMSD but their distribution is not uniform along the z axis. The deviation is largest at the edge on the rear side with a maximum of 0.7 Å at 0.4 ps due to the slightly increased ion temperature on the rear side (see Fig. 3) and higher structural flexibility at the surface [80]. These changes are only slight and consistent with a solid phase.

C. Laser irradiation above damage threshold

1. Overall changes within the first 3 ps

For laser irradiation with a fluence of 0.12 J/cm² above the damage threshold, laser ablation takes place. Figure 4 shows snapshots at selected times up to the first 3 ps. The rear surface structure at 0.33 ps, which is after the pulse has passed, has begun to be disordered. This is because stronger absorption occurs on the rear side due to the constructive interference as seen in the case of the fluence of 0.07 J/cm². Electrons then start to be ejected from the rear surface. At 0.6 ps, the rear surface has become more disordered or molten state, and more electrons have been ejected. The disorder has progressed to vaporization of ions by 1.0 ps. On the front side, the surface disorder and ejection of electrons have then occurred. As shown in the panel of 2.0 ps, the behavior subsequently

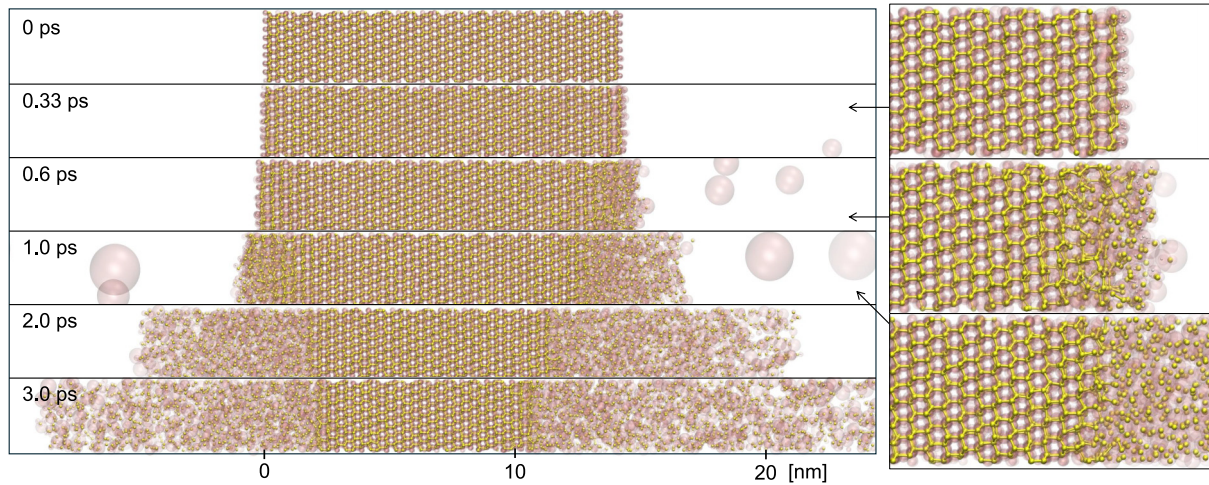


FIG. 4. Snapshots of electrons (translucent pink spheres) and ions (yellow small balls) at selected times up to 3 ps after laser irradiation with a fluence of 0.12 J/cm^2 .

continues at the rear side, and the similar behavior also occurs at the front side. After that, further vaporization continues at both surfaces, and roughly half of the film is ablated within 3 ps. It can be then seen that numerous electrons in the vaporized region are present either as unbound plasma electrons or as electrons accompanying the ejected ions, while the inner region retains the solid structure with a well-defined interface.

The spatial distributions of the number densities of electrons and ions at selected times are shown in Fig. 5(a). Both distributions decrease first from the rear side and then from the front side after a delay of several hundred femtoseconds,

as also seen in the snapshots in Fig. 4. At the same time, shoulder-like distributions consisting of ejected ions and electrons grow outward. Comparing the distributions of electrons and ions, closely similar shapes are maintained throughout the vaporizing process, but the distribution of electrons is a little lower than that of ions at surfaces and in the shoulder regions. Such similar shape is understandable as electrons and ions attract each other. The small difference can be explained by some amount of electrons being ejected soon after irradiation. As later shown, about 80 electrons have been ejected from the rear surface within 1.5 ps. This difference in the distributions between electrons and ions may be reflected as significant Coulomb interactions. It is discussed in Sec. III C 5.

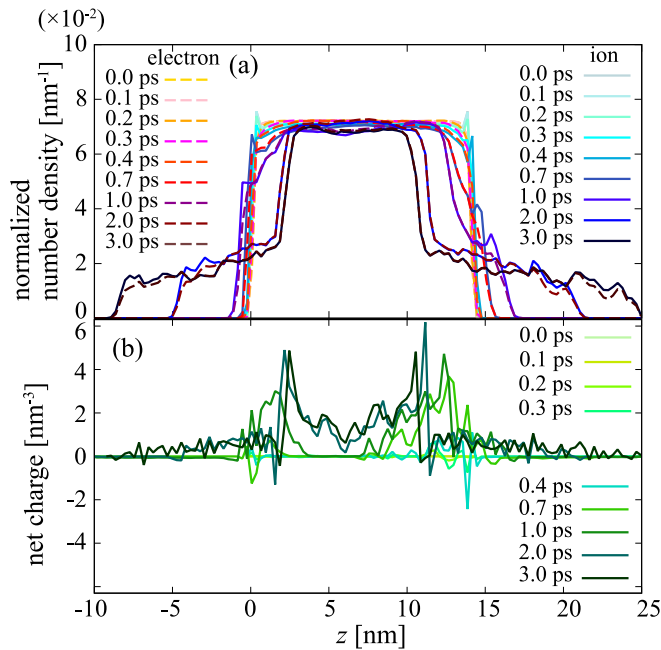


FIG. 5. (a) Normalized number density distributions of the electrons and ions and (b) distributions of net charge density per nm^3 (see Supplemental Material Sec. E for detailed definition [78]) along the z axis at selected times during and after laser irradiation with a fluence of 0.12 J/cm^2 .

2. Microscopic changes within the first 3 ps

To see the changes of state of the film, we examine the distributions of $\langle \Delta l(z, t) \rangle$, which reflects electronic states, at selected times as shown in Fig. 6(a). It stays below $0.3 \text{ \AA}$ up to 0.4 ps , remaining in the bonding state of the solid state, except at the rear surface side. Considering that $\langle \Delta l \rangle$ in the complete molten liquid state is around $0.8 \text{ \AA}$ as shown previously [39], the state at the rear surface showing around $0.5 \text{ \AA}$ can be considered in the process of bond breaking. The higher value at the surface is due to the destabilized state, and a sharp increase outside the surface is due to the ejected electrons. After 1.0 ps , $\langle \Delta l \rangle$ at the front side also exhibits a sharp increase. The rising positions at both sides then shift inward, indicating the molten or vaporized regions expand from both sides. The remaining solid region at 3.0 ps lies between 3 and 10 nm, though the ablation is still on going.

$\langle \Delta l \rangle$ in Fig. 6(a) is closely associated with the RMSD distribution of ionic positions shown in Fig. 6(b). Details of the RMSD calculation is written in Sec. E of Supplemental Material [78]. Correlating with $\langle \Delta l \rangle$, the deviation begins to rise at the rear edge and subsequently at the front edge. This behavior is attributed to the increased ion temperature and also to the higher structural flexibility at the surface [80]. The RMSD in the molten or vaporized regions expanding from both sides exhibits a significantly high value especially after

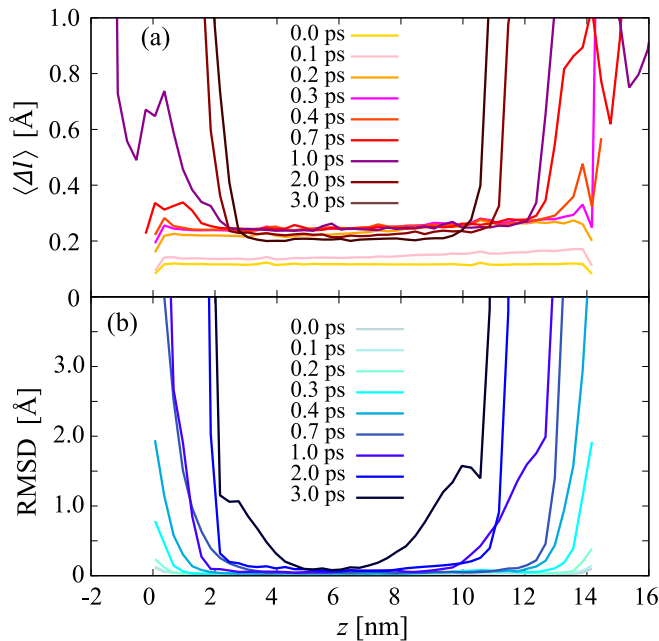


FIG. 6. Distributions of (a) the order parameter $\langle \Delta I(z, t) \rangle$ and (b) RMSD of ionic positions along the z axis at selected times during and after laser irradiation with a fluence of 0.12 J/cm².

0.4 ps, while that in the remaining solid phase region stays below 0.2 Å or up to around 2 Å at 3 ps possibly due to internal strain induced by expansion. These dynamics can be better understood by looking at the thermal behavior as shown in the next section.

3. Temperature dynamics within the first 3 ps

To figure out the energy flow, changes of the temperature distributions of electrons and ions are shown in Fig. 7. The electron temperature increases more on the rear side than on the front side at 0.2 ps due to the constructive interference during irradiation. When the pulse ends at about 0.27 ps, it reaches around 3000 K nearly uniformly, while the ion

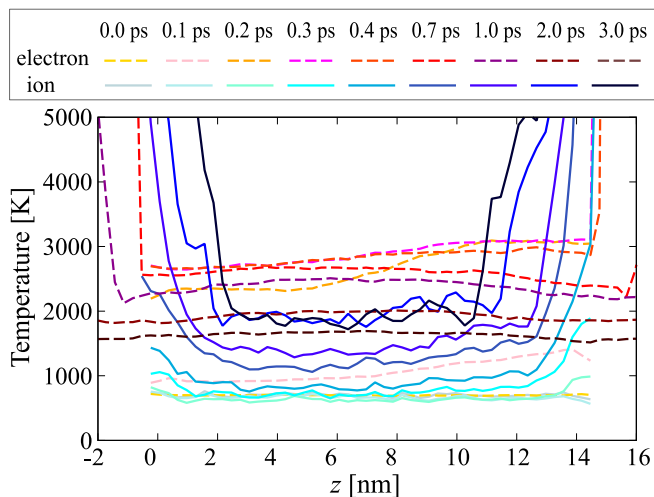


FIG. 7. Temperature distributions of electrons and ions along the z axis at selected times up to 3 ps during and after laser irradiation with a fluence of 0.12 J/cm².

temperature begins to rise and reaches to about 2000 K at the rear edge, corresponding to the initial rise of the RMSD at the surface [Fig. 6(b)]. This is caused by the energy relaxation from electrons. With using intense femtosecond laser pulse, as stated in literature [81], highly electronic excitation directly disrupts the chemical bondings, and the ions can then gain kinetic energy from the destabilized local state induced by the strong changes in atomic potential surface through this ultra-fast nonthermal process. This behavior involves the driving force of ion ejection.

The distributions of electron temperature outside the surface at 0.3 and 0.4 ps represent ejected electrons. When the initial electron is ejected from the rear surface at around 0.3 ps, the structure at the surface can still be somehow regarded as solid, based on the values of the order parameter and ionic RMSD shown in Fig. 6, though it is in a highly transient state. Once the electrons that have sufficiently high kinetic energies go out from the film, their radii relax along the slope of U_s^{ele} into delocalized forms in the open vacuum space, which results in the higher outside temperature owing to the increased p_s .

After 0.3 ps, the ion temperature near both surfaces increases rapidly as the energy relaxation from the electrons is accelerated. In general, structural defects and disorder exhibit an anomalously large electron-phonon coupling [82,83]. The ions at the disordered surface therefore can gain large kinetic energy from the heated electrons. In the present case, considering that the increase of ion temperature is quite steep at the surfaces after 0.4 ps and the well-defined interface moves inward, a detailed analysis would be necessary to understand this behavior, and it will be presented in Sec. III C 5. The regions at the high ion temperature are in the vaporized state, consisting of ejected ions, and correspond to the low-density shoulder region in Fig. 5(a). This could be the onset of a so-called phase explosion [69,72,73].

The electron temperature, on the other hand, is almost spatially uniform as electrons reach quasiequilibrium state much faster throughout both the vaporized regions and the film. The temperature in the regions decreases after 0.4 ps during the evaporation process. This could be caused by three factors of energy relaxation from electrons to ions, evaporative cooling, and adiabatic expansion of the vaporized region.

4. Electron emission

We now look into more details of ejection kinetics of electrons. The accumulated number of the ejected electrons, which is counted at $z \approx -9$ and 23 nm (i.e., 9 nm away from the initial surface positions) when they cross, is plotted in Fig. 8(a). That of ions is also plotted. The initial ejection of electrons occurs on the rear side at about 0.33 ps (corresponding to the panel of 0.33 ps in Fig. 4), and subsequently the ejection on the front side occurs at about 0.75 ps. The numbers on both sides increase for roughly a picosecond, but then they become almost unchanged indicating that the ejections of electrons have come to an end.

Figure 8(b) shows the z components of the ejected electron velocities up to 2.3 ps, where the positive values correspond to the ejected electrons from the rear surface and negative values to those from the front surface. As can be seen, the initial

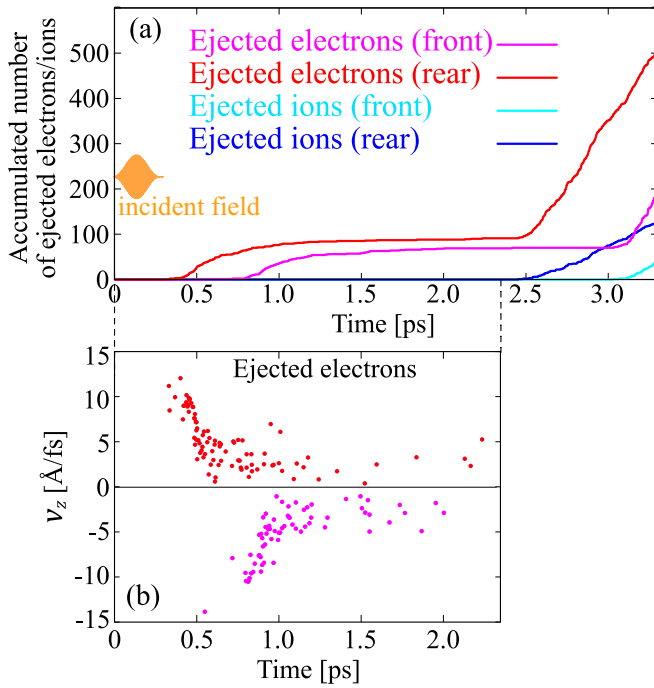


FIG. 8. Time evolution of (a) the accumulated numbers of ejected electrons and ions on the front and rear sides, where these are counted at $z \approx -9$ nm and 23 nm. (b) The z components of the velocities of the ejected electrons. The incident field is inserted as orange color in the panel (a) to indicate the irradiation interval.

groups on both the rear and front sides have higher velocities, but velocities of subsequently ejected electrons become lower, and the number decreases afterward. Since the pulse irradiation ends at about 0.27 ps, the initial electron ejection at about 0.33 ps is not attributed to the direct interaction with the electromagnetic field. In the present setup, the electric field of the incident wave is parallel to the film surface. The Coulomb force on the electrons due to the interaction with the incident field is not directed toward the outside of the film. Therefore, the electron ejection at the higher velocities in the initial groups is achieved by a sufficiently elevated electron temperature during photoexcitation. This, however, may not be solely a factor, since the electron temperature has already reached the maximum at the rear surface at 0.2 ps as seen in Fig. 7. The main change that occurs from then up to the initial ejection is the disordering of the rear surface [see Figs. 6(b) and 7]. This may open a channel for electron ejection, facilitating their passage with delocalizing (i.e., having an increased radius). That is, the initial electron ejection could proceed via a surface-disordering assisted transient thermionic emission mechanism.

After the initial higher velocity group, the velocities of subsequent ejected electrons are reduced [Fig. 8(b)]. This would be attributed to the reduced temperature of the electron system resulting from the evaporative cooling, the explosive adiabatic expansion, and the energy relaxation (see Fig. 7). At about 2.5 ps in Fig. 8(a), ejected ions together with electrons on the rear side, including the terminating ions, start to significantly increase nearly linearly. This is because numerous vaporized ions together with electrons reach the detection positions (note

that the onset of the ionic vaporization at the surfaces is earlier). Those on the front side also start to increase at about 3.1 ps.

As a supplementary check of the optical effect of the incident wave on the ablation behavior, we carried out a simulation without feedback from the material to the electromagnetic wave [i.e., the electric current density term in Eq. (3) was removed]. As expected, in contrast to Fig. 7, the electron temperature distribution during photoexcitation is quite flat, and the electron emission occurs at the front and rear sides almost simultaneously. This behavior can be explained by absence of constructive interference. In other words, it is confirmed that the higher electron temperature and initial electron emission at the rear side are caused by the constructive interference due to the optical effect. Details are provided in Sec. C of the Supplemental Material [78].

5. Driving force of ion ejection

We here analyze the driving force of ion ejection. As indicated by the rapid increase of the ion temperature shown in Fig. 7, the ions at the surface start to be explosively ejected. At the beginning, the bonding structure becomes destabilized due to the high excitation of electrons. Then, roughly two factors are considered to drive ion ejection. One is the interaction with electrons. Since the electrons have high kinetic energy after absorbing the light field, they can push the ions outward or pull them as the electrons are ejected. This mechanism is electron-driven ion acceleration, often referred to as the electron pressure model [60–64] or the electron pulling model [59,84]. The other is the Coulomb repulsive force between positively charged ions, known as the Coulomb explosion model [55–58]. The missing electrons, which results from the ejection of electrons, can induce strong local Coulomb repulsions. Figure 5(b) shows the spatial distribution of the net charge density. This indicates that the net charge is indeed positive, especially near the surfaces, and becomes larger at later times. This implies that the net Coulomb repulsion at the surface pushes the ions out.

To facilitate the force analysis, the ions are grouped into layers according to their z coordinates on the rear side. Figure 9 shows the averaged z coordinate of the ions in each surface layer as a function of time, where the first layer refers to the group of $\text{Si}^{(\text{cap})}$ [terminating atoms(ions)], the second layer to the group of outermost Si ions, and subsequent layers to the inner Si groups in order. One can see that the ion groups move outward in order at a similar speed, where the second layer group moves the fastest. Since the first-layer [$\text{Si}^{(\text{cap})}$] group moves more slowly than the second (outermost Si) layer group, it is overtaken by the second layer at around 0.8 ps. Note that the masses of the terminating ion and Si ion are set to be the same. This suggests that the force on the second-layer group is larger than that on the first-layer group and plays a more dominant role in driving the ion ejection. We therefore focus on the first- and second-layer groups for the analysis.

The analysis is conducted by decomposing the z component of the force acting on the ions. In the ejection process, the ions can form different charge states by capturing unbound electrons. For the case of silicon, the bare ion, Si^{4+} , can bind to nearby unbound electrons, forming lower charge states

In the case of the total force, ΔF_{tot} is close to F_{tot} as $F_{\text{tot}}(t = 0)$ is nearly zero. For each component, a positive ΔF_{α} drives the ejection, whereas a negative one inhibits it. Hereafter, the force difference is referred to simply as force unless otherwise noted.

To distinguish between the electron-driven ion acceleration model and the Coulomb explosion model, we group the decomposed force components into those associated with the two models as

$$\Delta F_{\text{ele-dri}} = \Delta F_{R/\text{cl}}^{\text{ele}} + \Delta F_{R/\text{cl}}^{\text{ion}} + \Delta F_{R/\text{rep}} + \Delta F_{L/\text{rep}}, \quad (36)$$

$$\Delta F_{\text{cl-exp}} = \Delta F_{L/\text{cl}}^{\text{ion}} + \Delta F_{L/\text{cl}}^{\text{ele}}. \quad (37)$$

See Sec. II F 4 for the notations of the force components. The force component of the electron-driven ion acceleration model, $\Delta F_{\text{ele-dri}}$, is composed of the Coulomb attraction from a right-side electron, i.e., an outward pulling force ($\Delta F_{R/\text{cl}}^{\text{ele}}$), the Coulomb repulsion from a right-side ion, which acts to push inward and to screen the electronic Coulomb attraction ($\Delta F_{R/\text{cl}}^{\text{ion}}$), and the interelectronic repulsion from the right and left sides, acting through the Si core electrons and the bound electrons in the complex ($\Delta F_{R/\text{rep}} + \Delta F_{L/\text{rep}}$). The force component of the Coulomb explosion model, $\Delta F_{\text{cl-exp}}$, is composed of the Coulomb repulsion from a left-side ion, i.e., an outward repulsive force ($\Delta F_{L/\text{cl}}^{\text{ion}}$), and the Coulomb attraction from a left-side electron, which acts to pull inward and to screen the interionic Coulomb repulsion ($\Delta F_{L/\text{cl}}^{\text{ele}}$).

Figure 10(b) shows $\Delta F_{\text{ele-dri}}$ and $\Delta F_{\text{cl-exp}}$, for the first-layer group. In the initial period up to 0.2 ps, $\Delta F_{\text{cl-exp}}$ shows a slight positive value. As seen in Fig. 10(a), the component responsible for this increase is $\Delta F_{L/\text{cl}}^{\text{ele}}$. This suggests that the inward pulling force from electrons on the left side is weakened as a result of the bond destabilization. After 0.2 ps, however, $\Delta F_{\text{ele-dri}}$ increases positively, where the component responsible for this increase is $\Delta F_{R/\text{cl}}^{\text{ele}}$ [Fig. 10(a)]. This corresponds to the outward pulling force from electrons on the right side, that is, force from the electrons being ejected or from the electrons that have appeared on the surface. Thus, the pulling attractive force acting by the ejected electrons serves as the driving force for the ejection of the terminating atoms in the first-layer group. $\Delta F_{\text{cl-exp}}$, on the other hand, turns negative because the Coulomb repulsion component $\Delta F_{L/\text{cl}}^{\text{ion}}$ [Fig. 10(a)] is reduced as a result of the increased interionic distance from the left layer.

The force difference components corresponding to two models for the second-layer group are plotted in Fig. 10(d). Contrary to the result of the first-layer group, $\Delta F_{\text{cl-exp}}$ shows a much larger positive increase. As seen in Fig. 10(c), $\Delta F_{L/\text{cl}}^{\text{ele}}$ is the component responsible for this increase. This indicates that the inward pulling force from the left-side electrons is greatly weakened, first by the bond breaking in the initial period and later by the ejection of electrons that were initially located on the left side. This corresponds to a reduction in the electronic screening effect. As a result of this reduced electronic screening, the Coulomb repulsion from the left-side ions exceeds the inward pulling force (even though $\Delta F_{L/\text{cl}}^{\text{ion}}$ decreases by the increased interionic distance), and then $\Delta F_{\text{cl-exp}}$ becomes positive. On the other hand, $\Delta F_{\text{ele-dri}}$ shows large negative increase. This behavior is explained by the reduction of $\Delta F_{R/\text{cl}}^{\text{ele}}$ resulting from the decrease in the number of

the right-side electrons due to the ejection and simultaneously less increase of the inward pushing force from the right-side ions of $\Delta F_{R/\text{cl}}^{\text{ion}}$ as the first-layer group is ejected. Thus, since the positive increase of $\Delta F_{\text{cl-exp}}$ is stronger than the negative increase of $\Delta F_{\text{ele-dri}}$, positive total net force drives the ejection of the second-layer group.

In comparing the obtained mechanisms, the ion ejection of the first-layer group is caused by the electron-driven mechanism, whereas that in the second-layer group is driven by the Coulomb explosion mechanism. The total net force on the second-layer group is stronger than that of the first-layer group, which results in weaker ejection of the outermost terminating ions than the others, as seen in Fig. 9. The ejections of the other inner-layer groups are also driven as the same manner of the second-layer group (see Fig. S5 in Supplemental Material Sec. D [78]), which is consistent with the positive net charge at the surface even after some layers are ejected [Fig. 5(b)]. These results suggest that when a layer is ejected and the underlying layer becomes new surface, electrons near the newly exposed surface are ejected as long as they possess sufficiently high energy. This leads to a net positive charge at the new surface and induces sequential Coulomb explosions. Thus, the Coulomb explosion plays dominant role for the ion ejection in the present system and condition.

6. Dynamics up to 15 ps

To see how it evolves after 3 ps, we show the snapshots every 3 ps up to 15 ps in Fig. 11. At 3 ps, explosive evaporation has already occurred at both surfaces as also shown in Fig. 4. The vaporized species, consisting of ejected ions with accompanying electrons and unbound plasma electrons, spread and expand toward the front and rear directions. They gradually become less dense, while the thickness of remaining film remains almost unchanged after 6 ps. During the expansion, one can see that small cavities have begun to appear in the vaporized region at 9 ps. The cavities grow larger after that, which leads to an inhomogeneous vaporized region and further separation into denser regions and small bubbles or vacuum regions. Our simulation at 15 ps exhibits somehow mixed spallation and fragmentation on the way of expanding. According to molecular dynamics calculation studies [69,85,86], behaviors in the phase explosion quite depends on the laser fluence. Spreading of gaseous atoms from the outmost surface, spallation, and fragmentation have been observed with increasing fluence. It would be future work for our simulation to evaluate fluence-dependent phase and plasma behaviors using larger system size. On the other hand, the remaining film part, whose thickness is almost unchanged after 6 ps, slightly shifts to the left. This motion is driven by the stronger explosive vaporization occurring at the rear surface compared with the front surface.

Some detailed dynamics up to 15 ps is shown in Fig. 12. Due to the ion ejection, the thickness of the remaining film decreases. The number of ions in it is plotted as a function of time in Fig. 12(a), where the remaining film is defined as the largest part in which the interionic distances are within 2.6 Å (the optimal Si-Si bond length in the eFF model is about 2.3 Å). It starts to decrease at around 0.5 ps, and continues to decrease smoothly. After around 2 ps, it gradually stops

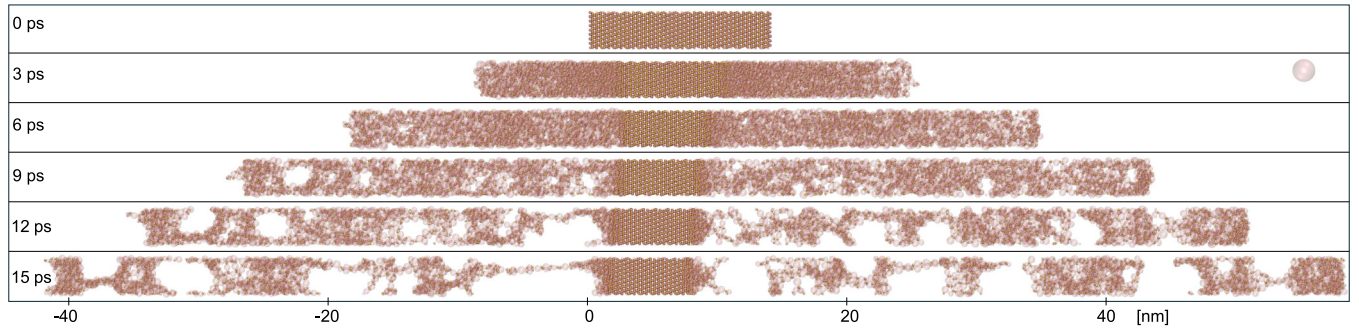


FIG. 11. Snapshots of electrons (translucent pink spheres) and ions (yellow small balls) at selected times up to 15 ps after laser irradiation with a fluence of 0.12 J/cm^2 .

decreasing by about 6 ps. This is because a large portion of the absorbed light energy is used for the explosive vaporization. The electrons and ions are cooled by the evaporation and the expansion after 3 ps as shown in Fig. 13, and as a result, they no longer have enough energy for ejection. This is reflected in the accumulated number of ejected ions plotted in Fig. 12(b) as a gradual approach to a plateau. Looking at the z components of velocities of ejected ions in Fig. 12(c), the velocities of ejected ions are gradually reduced in the picoseconds scale.

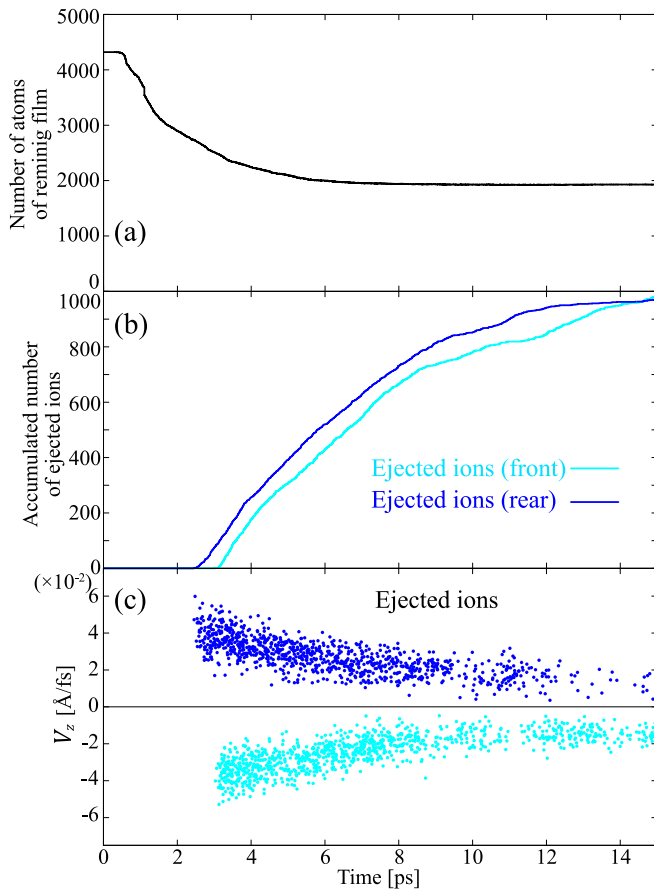


FIG. 12. Time evolution up to 15 ps of (a) the number of atoms (ions) in the remaining silicon film and (b) the accumulated number of ejected ions on the front and rear sides, where these are counted at $z \approx -9 \text{ nm}$ and 23 nm . (c) The z components of the velocities of the ejected ions.

IV. SUMMARY AND MICROSCOPIC MECHANISMS

We developed the molecular simulation that combines Maxwell equations and the semiclassical eFF model, referred to as the Maxwell + eFF-MD simulation. This incorporation of light wave into a force-field based electron/ion particle model may be an interesting attempt as it enables us to simulate interaction dynamics among electrons, ions in a condensed matter and electromagnetic field, especially in a high-energy region. The method is applied to a silicon thin film. The optical linear response using a weak impulsive pulse was examined first, and the calculated reflection, transmission, and absorption spectra were confirmed to reasonably exhibit thickness and surface effects.

We next examined a simulation using intense 100-fs pulsed laser irradiation with fluence of 0.12 J/cm^2 , and the explosive dynamics at the electronic and ionic level in the laser ablation process were captured. From the simulation analyses, the mechanism of the initial ablation stage is as follows (the schematic summary of the microscopic mechanisms obtained from the present simulation is shown in Fig. 14): During the electrons are excited through one-photon absorption by the interaction with a propagating electromagnetic field, the

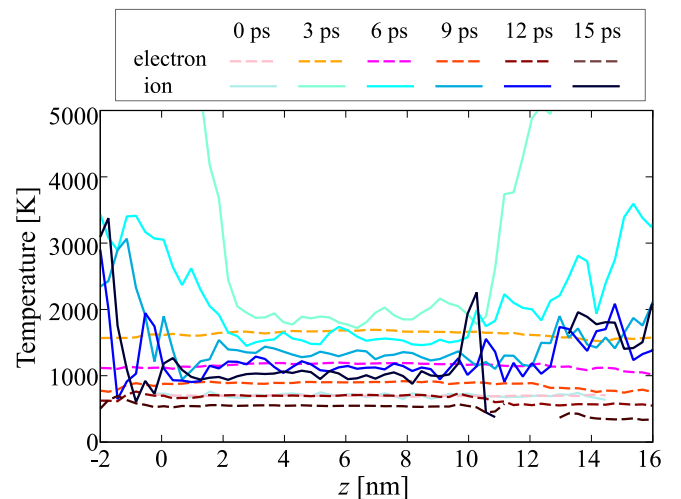


FIG. 13. Temperature distributions of electrons and ions along the z axis at selected times up to 15 ps after laser irradiation with a fluence of 0.12 J/cm^2 .

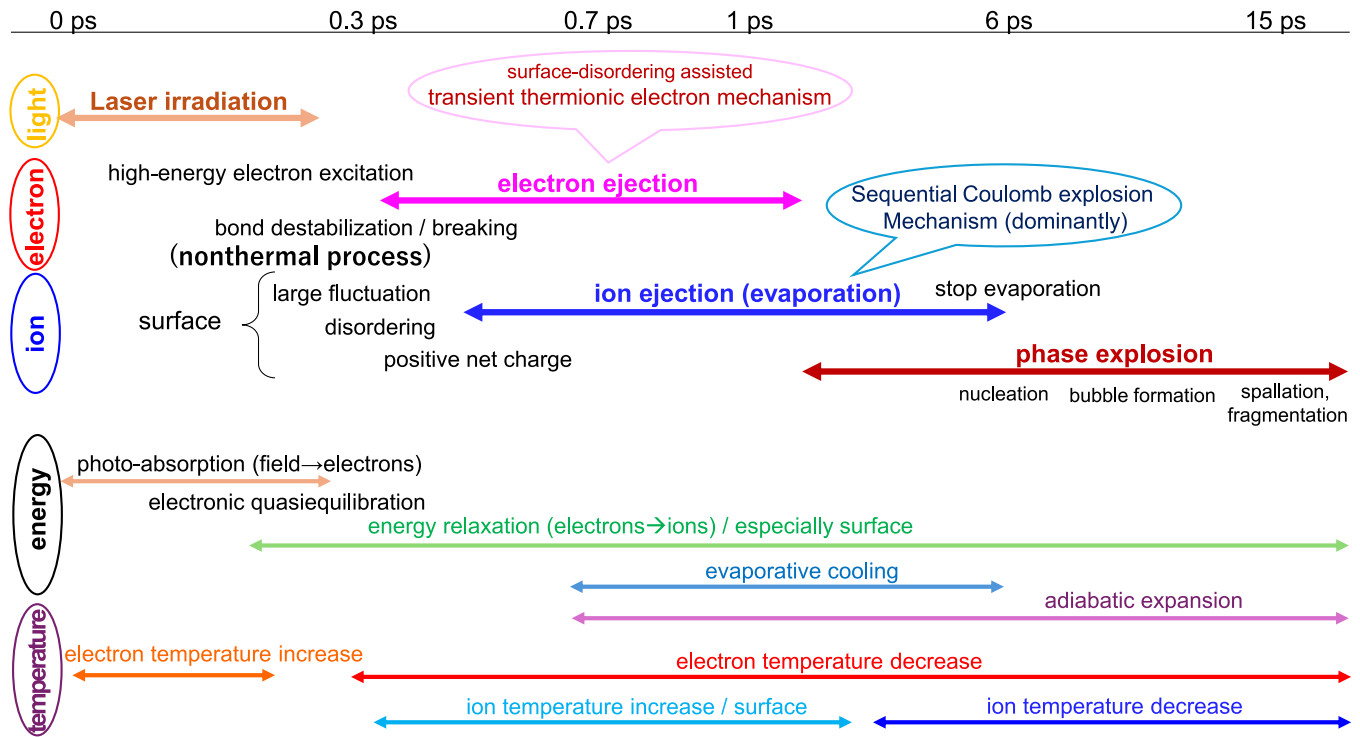


FIG. 14. Schematic summary of microscopic mechanisms during the laser ablation process obtained from the present simulation.

electron temperature is elevated up to several thousand kelvin, but not uniformly, being higher on the rear surface side than on the front surface side, owing to constructive interference in the present setup. The ion temperature subsequently begins to rise at the rear surface due to energy relaxation from electrons in several hundred femtoseconds through ultrafast nonthermal process. That is, in this process, absorption of the intense laser energy leads to instability in electronic bondings, which causes significant change in interatomic interaction inducing larger structural fluctuation or disorder especially at the flexible surfaces. During these processes are on going and after the pulse has passed, the electron temperature becomes uniform along the z axis due to the rapid electron quasiequilibration. The electrons with sufficiently high kinetic energy are at last ejected from the rear surface possibly with assistance of the opened channels on the disordered surface. This mechanism is kind of transient thermionic emission occurring in highly nonequilibrium dynamics. When the electrons are ejected, they pull the terminating ions of the outermost surface atomic layer, leading to their ejection. At the same time, missing electrons near the surface, which result from the electron ejection, further disorder the structure and also reduce the screening of the Coulomb interaction. As a result, local interionic Coulomb repulsion, in which the net-charge becomes positive, serves as the driving force for the explosive ejection of Si ions, corresponding to the so-called Coulomb explosion model. The ions are thus accelerated gaining high kinetic energy near the surfaces and then start to be vaporized. The sequential Coulomb explosions occur on the newly exposed surface due to the electron-ejection-induced net positive charge. These

behaviors occur at the front surface a few hundred femtoseconds later. As the ions are vaporized, the electron temperature decreases. This decrease is attributed to evaporative cooling and adiabatic expansion. In addition, ion-electron energy relaxation contributes to the cooling, as it is promoted in the disordered and damaged structure. The ejection velocities of electrons are then lowered, preventing the further ejection alone. The remaining electrons accompany the ejected ions or are present as unbound plasma electrons in the vaporized region thereafter. Further expansion leads to less dense vapor, and small cavities begin to appear. As the cavities grow larger, the vaporized region is induced into an inhomogeneous vapor/vacuum separation after ten picoseconds through the phase explosion process.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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