Femtosecond laser processing of germanium: an ab initio molecular dynamics study

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Received 5 June 2013, in final form 26 September 2013
Published 19 November 2013
Online at stacks.iop.org/JPhysD/46/495108

Abstract
An ab initio molecular dynamics study of femtosecond laser processing of germanium is presented in this paper. The method based on the finite temperature density functional theory is adopted to probe the structural change, thermal motion of the atoms, dynamic property of the velocity autocorrelation, and the vibrational density of states. Starting from a cubic system at room temperature (300 K) containing 64 germanium atoms with an ordered arrangement of 1.132 nm in each dimension, the femtosecond laser processing is simulated by applying a Nosé–Hoover thermostat to the electronic subsystem for ∼100 fs and continuing with a microcanonical ensemble simulation of ∼200 fs. The simulation results show solid, liquid and gas phases of germanium under adjusted intensities of the femtosecond laser irradiation. We find that the irradiated germanium is distinguishable from the usual germanium crystal by analysing their melting and dynamic properties.

(Some figures may appear in colour only in the online journal)

Nomenclature

| Symbol | Definition |
|--------|------------|
| c      | conversion coefficient, eV K⁻¹ |
| d      | length of the simulation system in one direction, Å |
| k_B    | Boltzmann constant, 1.38 × 10⁻²³ J K⁻¹ |
| E      | atomic-scale energy, Ha |
| E_H    | ion–ion Coulomb energy, Ha |
| f_i    | Fermi–Dirac occupation number |
| J      | femtosecond laser fluence, J cm⁻² |
| M      | atomic mass, a.u |
| N_e    | number of electrons |
| N_i    | number of ions |
| r_i    | position of the atom i |
| R      | ionic position vector, Bohr |
| T      | temperature, K |
| v      | velocity, Bohr/a.t.u |
| V      | potential term in the Hamiltonian, Ha |
| V_i    | three components of the velocity v_x(t), v_y(t) and v_z(t) |
| ψ_i   | one-electron eigenstates |
| Φ      | electronic free energy, Ha |
| Ω      | ground potential for an interacting spin Fermi gas, Ha |
| H      | one electron Hamiltonian |
| ν      | vibrational frequency of atom, s⁻¹ |
| ρ      | electron density |
| ρ xc   | exchange and correlation |
| e      | electron |
| I      | ion |
| vol    | volume of the modeled system |

1. Introduction

Femtosecond laser processing has been widely used in the fabrication process of cutting-edge semiconductor integrated circuits (ICs) and nanoelectromechanical systems (NEMS). Photolithography, serving as a conventional approach to fabricate the microstructures, has been a predominant technique since the emergence of semiconductors. However, traditional photolithography suffers from the drawbacks of
high cost and complex treatment for the masks with the miniaturization of structure due to optical diffraction in nanoscale. Femtosecond laser processing (nanolithography), due to its inherent advantages of maskless super resolution [1], offers a potential solution for the high mask cost. In addition, compared with nanosecond pulses, the femtosecond laser has the advantages of high peak power intensity and a relatively smaller heat-affected zone, which make it ideal for a wide range of applications in other fields of material sciences [2–6]. In many engineering applications, ranging from laser micromachining to surface treatment, the femtosecond laser material interaction has become an increasingly hot topic. The laser intensity of a femtosecond laser can even be up to \(10^{21}\) \(\text{W m}^{-2}\) [7], which results in the breaking down of traditional phenomenological laws. Hence, for the purpose of achieving a better comprehension and understanding of femtosecond laser nanolithography, it is of great necessity to investigate the melting and dynamic effects related with energy transfer and conversion in the atomic scale.

The laser material interaction has attracted considerable attention in the past two decades due to both the relevant technological importance and theoretical interest. Because the characteristic times of the energy carriers are comparable to the characteristic energy excitation time, there are two competing interpretations to the thermal mechanical phenomena: one is the plasma annealing, another one is thermal annealing. The plasma annealing describes the microscopic mechanism as the lattices of semiconductors directly transform into a disordered state long before the system becomes thermally excited. For semiconductors, like silicon, phonons are the major energy carriers. Because the free electron density in a semiconductor is much lower than that in a metal, the participation of electrons can be neglected. The mechanism under femtosecond laser irradiation is generally regarded as an athermal transition, which mainly softens the interatomic bonds in the time domain that is long before the conventional thermal transition caused by heat transfer from the electrons to phonons [8]. After femtosecond laser irradiation, the electrons transform from the bonding to antibonding states by depleting the bond charges. In other words, when the stage of disordering of the latter happens, the ion temperature still remains at room temperature. A tight-binding model was introduced to study the effects of a dense electron–hole plasma on the instability of carbon, silicon and germanium [9, 10]. The other alternative explanation is the thermal melting, which requires the direct energy transfer between the excited electrons and the ions. Due to the electron–phonon coupling, the large amount of excited electron energy transfers to ions within the picoseconds time domain, which causes thermal melting of the lattice.

For the femtosecond laser, the pulse duration is shorter than the electron–lattice thermalization time (in the order of picosecond). Because the excited electrons do not have sufficient time to transfer a large amount of energy to the ions, plasma annealing seems to be the dominating mechanism. The ultrashort laser pulse makes it possible to excite the electronic states of a solid long before the appreciable energy transporting to the lattice vibrational states. Shank et al. [11] showed transition from crystalline order to disorder with melting of the surface occurring in less than 1 ps under 90 fs laser illumination on silicon. Rousse et al. [12] reported the nonthermal melting process in InSb at femtosecond resolution by using ultrafast time-resolved x-ray diffraction. An atomic-scale visualization of internal dynamics presented by Lindenberg et al. [13] demonstrated the nonthermal transition from crystalline solid to disordered liquid. Apart from an experimental investigation, by employing first principles calculation, Zijlstra et al. [14] showed the nonthermal melting of InSb induced by a femtosecond laser based on dramatic changes of transverse acoustic phonons at the boundary of Brillouin zone. Subsequently, anharmonic effects which dominate the atomic motions for times greater than 100 fs were studied [15]. Moreover, the relationship of thermal phonon squeezing under low fluence femtosecond laser irradiation and the same pathways of atomic motion at the first stages of nonthermal melting was reported by Zijlstra et al. [16], which originated from the femtosecond-laser-induced softening of the interatomic force constant. They concluded that the phonon squeezing played the role of the precursor to nonthermal melting with the increasing of laser fluence. Threshold intensities of nonthermal phase transition for semiconductors (such as Si and InSb) were reported by utilizing semiclassical electron-radiation-ion dynamics (SERID) [17]. In this work, the \textit{ab initio} molecular dynamics simulation method based on finite temperature (FT-DFT) is used to simulate the femtosecond laser interaction of germanium. The approach has already been employed to simulate the laser melting of silicon and graphite [18, 19]. Since the FT-DFT method incorporates self-consistently the effect of thermalized electronic excitations and a fractionally occupied state, it can reasonably and accurately describe the electronically hot system. The original work of \textit{ab initio} molecular dynamics of excited electrons was presented by Alavi et al. [20]. We carried out a simulation with different incident laser intensities of \(\sim\)100 fs time duration. All the cases started from germanium crystal at room temperature (300 K). To obtain the final equilibrium state of the electronic and ionic subsystem, we monitored the temperature of the nucleus as output during the entire simulation process. The phase changes from the solid state to liquid state (melting point of Ge: 1211.40 K) and gas phase (evaporation point of Ge: 3106 K) were validated from microstructure property, thermal motion and dynamics feature analyses.

2. Theory and method

2.1. \textit{Ab initio} molecular dynamics based on FT-DFT

The concept of the finite temperature version of the density functional theory was originally proposed by Mermin [21] when he referred to the thermal properties of electron gas. The functional introducing the finite electron temperature of effects into the DFT is

\[
\Omega [\varphi_i(r)] = E^{\text{KS}}[\varphi_i(r)] - T_i S_i, \quad (1)
\]

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where $E^{KS}[\varphi_i(r)]$ is the Kohn–Sham energy functional at $T_e = 0$ and $S$ is the entropy, which can be expressed as

$$S = -k_B \sum_i [f_i \ln f_i + (1 - f_i) \ln (1 - f_i)].$$

(2)

For the specific case of non-interacting fermions, the grand potential expression is

$$\Omega(\mu, V, T) = -k_B T \det^2 \left(1 + e^{-\frac{\delta \Omega_{xc}}{\delta \rho}}\right)$$

(3)

where $\mu$ refers to the chemical potential acting on the electrons and $\Omega$ is the one electron Hamiltonian $\Omega = -(\hbar^2/2m)\nabla^2 + V(r)$. The power of two is because of the spin multiplicity. The effective density dependent potential term in the Hamiltonian is expressed as

$$V(r) = -\sum_i \frac{Z_i e^2}{|R_i - r|} + V_{\text{H}} + \frac{\delta \Omega_{xc}}{\delta \rho(r)}.$$  

(4)

The free energy $F$ is a functional of the electron density $\rho(r)$, the Fermi-Dirac occupation number $f_i$ of the one-electron eigenstates $\varphi_i(r)$ and the chemical potential $\mu$. Recalling the mathematical relationship $\delta \rho(r) = 2 N$ in thermodynamics, we can get the average spin number. Therefore, the sum of the Helmholtz energy $[20]$ of one electron of density $\rho(r)$ and the ion–ion Coulomb energy $E_{\text{ion}}(R^N)$ is

$$F = \Omega + \mu N_e + E_{\text{ion}}(R^N),$$

(5)

where $\Omega$ denotes the grand potential for an interacting spin Fermi gas within DFT. In order to obtain the correct total electronic free energy of the interacting electrons, the extra terms have to be included in $\Omega^{KS}$, namely

$$\Omega = -\frac{2}{\beta} \ln \det \left(1 + e^{-\delta \Omega_{xc}/\delta \rho} \right) - V_{\text{H}} - \int \rho \left(\frac{\delta \Omega_{xc}}{\delta \rho(r)}\right) dr + \Omega_{xc}$$

(6)

where $\beta = 1/k_B T_e$ refers to as the electron temperature parameter and $\Omega_{xc}$ is the finite temperature exchange correlation grand potential functional.

The electron density is

$$\rho(r) = \sum_i \varphi_i(T) |\varphi_i(r)|^2$$

(7)

and the occupation number is

$$f_i(T) = \frac{f_i(0)}{1 + e^{-\frac{\delta \Omega_{xc}}{\delta \rho}(\varphi_i^{KS} - \mu)}}.$$  

(8)

where $\varphi_i^{KS}$ is the Kohn-Sham eigenvalues and $f_i(T)$ is the Fermi-Dirac occupation number in the grand canonical ensemble.

The optimization for the specific atomic configuration can be realized by adopting the Lanczos algorithm [22]. After the electron density $\rho(r)$ is obtained, the dynamic simulation is performed based on the optimization of the electron density at every time step. Then, the Hellmann-Feynman forces acting on the nuclear can be calculated via the differentiation of $F$ with respect to the ion coordinates:

$$F_i = -\nabla_i F.$$

(9)

Eventually, we can perform molecular dynamics simulation for the system with various temperatures of electrons.

2.2. Modelling and simulation

The $ab$ initio molecular dynamics simulation was started with germanium crystal at room temperature ($300 \text{ K}$). The CPMD package 3.15.3 [23] based on plane-wave pseudopotential implementation of FT-DFT and incorporating self-consistently the effects of thermal electronic excitations and fractionally occupied states was used. As introduced in section 2.1, a certain method is particularly congruent to deal with the electronically hot problems. A cubic system containing 64 germanium atoms were modelled with lattice constant 11.316 Å at x-, y- and z-directions, which corresponds to the density of germanium at 5.323 g cm$^{-3}$. The Γ point used to sample Brillouin zone of the molecular dynamics supercell. The simulation time step was set 4 a.u ($0.096755$ fs) to obtain integration of the total energies of freedom. The exchange correlation in our calculation was represented by the local density approximation (LDA) [24]. As pointed out by Silvestrelli et al. [25], the LDA underestimates the energy gap and the Γ point of the supercell used in FT-DFT simulation merely gives a poor representation of the density state condition band. Nevertheless, the LDA well describes the antibonding character of the conduction states and only gross features of the conduction band are relevant at high levels of excitation. We adopted the norm-conserving pseudopotentials with the Stumpf–Gonze–Schaeffler [26] pseudopotential method [27]. Periodic boundary conditions were applied in all three directions of the primitive cell of diamond cubic crystal structure. In our simulation, all cases adopted the cutoff of 35 Ry to expand the electronic orbitals in plane waves. The single particle electronic states were set as 200 to take all the levels of electronic excitation into consideration.

In order to perform the FT-DFT simulation, wavefunction optimization and geometric optimization were performed first to calculate the electronic structure of the system and the optimization results showed the cutoff of 35 Ry is sufficient enough to get the converged energies. After obtaining the optimized electronic structure, all the cases were run for 1000 time steps at room temperature ($300 \text{ K}$) with Nosé–Hoover [28] thermostat imposed on each degree of freedom for both electrons and nuclei, so that the electronic subsystem and the ionic subsystem could reach a sufficient equilibrium state before laser irradiation. The simulation time of femtosecond laser irradiation locates in the subpicosecond domain, which corresponds to a nonequilibrium population of the excited ‘hot’ electrons with a still ‘cold’ atomic lattice [29]. In our simulation, due to the fact that the estimated relaxation time for the electron–electron interaction ($\sim 10$ fs) is much shorter than the electron–ion interaction ($\sim 1$ ps) and ion–ion interaction ($\sim 10$ ps), the
The evaluation of electron temperature was based on the Maxwell–Boltzmann distribution of electron gas

\[ \langle E \rangle = \frac{3k_B}{2} \langle T \rangle = c \langle T \rangle \quad (10) \]

where \( c \) is a conversion coefficient from electron temperature of 1 K to average electron energy 8.6173 \( \times 10^{-5} \) eV. From the engineering perspective, with regard to femtosecond laser material processing, laser pulse duration and laser fluence (intensity) are two crucial parameters to characterize a femtosecond laser. In this study, the instant incident of laser fluence can be expressed by the energy increment of an electron subsystem:

\[ J = \frac{N_e N_i c \Delta T}{d_x d_y} \quad (11) \]

where \( N_i \) and \( N_e \) refer to the number of atoms included in the system and the number of electrons circling around one germanium nuclei; \( c \) is the conversion coefficient from electron temperature to average electron energy; \( \Delta T \) is the electron temperature increase induced by laser irradiation; and \( d_x \), \( d_y \) are the width and length of the modelled system. The calculated average electron energies, laser fluences and laser intensities are listed in table 1.

### 3. Results and discussion

#### 3.1. Ion temperature evolutions

We calculated the temperatures of the ionic subsystems along with the MD simulation for all of the cases. As is shown in figure 1, the ion temperatures exceed the melting point and evaporation point under the electron irradiation conditions at temperatures of 25 000 K and 50 000 K. We calculated the temperature of ions according the following definition

\[ T_i = \frac{2\bar{E}_i}{3(N-1)k_B}. \quad (12) \]

As we can see from figure 1, the lattices remain at relatively lower temperatures in the first 1000 time steps of laser irradiation in all cases.
irradiation. When the condition of femtosecond laser interaction is imposed, the relatively low temperature states of the ions remain for about 200 time steps (~0.2 fs) and then are followed by slow temperature increments from 1200 to 1500 time steps. After 1500 time steps, the ion temperatures show abrupt increases, especially for cases of the electronic subsystems with relatively higher energies. The advents of ion temperatures exceeding the melting and boiling points are also early for the electronic systems with higher temperatures than those with lower electron temperatures. After the temperatures of the ion subsystems increase to certain values, they stayed and oscillated in small ranges at temporarily equilibrium states with the electron subsystems. The same sort of kinetic energy (ion temperatures) responses to various intensities of femtosecond lasers are also reported in [29].

The temperature curve (1000–4000 time steps) for the case of 20000 K is distinctly different from that of 25000 K, which indicates that the 20000 K femtosecond laser almost cannot make the ions break most of their connecting valence bonds and they just keep oscillating wildly around their equilibrium positions. The same condition of femtosecond laser distinct threshold of 0.15 J cm\(^{-2}\) that enables the strong excitation and nonthermal process was experimentally measured for femtosecond processing of gallium arsenide [32]. It is not definite to draw the final conclusion that the ions will still keep at low temperatures for the case of electron temperature 20000 K, with the time duration to picosecond time scale. As pointed in Lindemann’s law [33], once the vibrational amplitude reaches up to 10% of the nearest neighbour distance, the vibration will disrupt the equilibrium crystal lattice and the melting phenomenon eventually takes place. The short simulation period could not reveal the melting phenomena for this case. Nevertheless, we can find that even though the simulation process lasts for ~0.3 ps, the temperature evolutions for the seven cases still distinguish from each other and the ion temperatures are much lower than the corresponding electron temperatures for all the cases. The phenomena can be interpreted from two aspects. On the one hand, the incident energy heats the electrons more strongly than the ions. On the other hand, atoms and ions are much heavier than electrons, which leads to the inefficient thermal energy transfer in a two-body collision because the masses are dissimilar. Moreover, as computed in table 1, the laser fluence exciting electron temperature to 60000 K is 0.1316 J cm\(^{-2}\), which is in the same order of magnitude as reported for the femtosecond laser ablation threshold fluence (0.2 J cm\(^{-2}\)) for silicon [34] and 0.17 J cm\(^{-2}\) for graphite films [35].

3.2. Free energy calculation

The quantities of free energies of the simulation systems were recorded to get a further insight into the changes of the microsystem. The Fermi-Dirac distribution was used for the purpose of filling the electronic states as a function of the temperature in the free energy functional calculation. Figure 2 shows the free energies of the system under different femtosecond laser irradiations. With the increasing laser energy intensities, the free energy drops by a greater range and stays at lower energy values. To get more explicit results, the detailed evolution curves of each case are shown in figure 3. The curves for free energies correspond to the ion temperature profiles are shown in figure 1. It means that while there is a free energy drop (see figure 3), there is an increment of the ion temperature (see figure 1). This kind of trend can also be found in the simulation result of silicon [25]. The comparisons among figures 3(a)–(d) demonstrate that even though the electron temperatures induced by the incident laser are tens to hundreds times higher than the ion temperature, the electronic-ionic energy exchange cannot happen instantaneously and efficiently for some cases where the electron temperatures are lower than a criteria (see the 20000 K and 30000 K cases). Additionally, the capability of the system to absorb external laser energy is also affected by the structural changes and the dependency of the absorbed energy on the laser intensity is nonlinear [36].

3.3. Structural change due to electron–ion interaction

To understand the thermal effect of femtosecond laser nanolithography, structural change is the primary parameter to evaluate the results of irradiated germanium. The radial distribution function (RDF) \(g(r)\) describes how the density varies as a function of distance from a reference particle. It is also referred to as pair distribution function or pair correlation function, which describes how, on average, the atoms in a system are radially packed around each other. As an important structural characteristic of crystal germanium, we computed the RDF based on the trajectories of atoms produced at different simulation stages from the initial equilibrium state at room temperature to the subsequent laser irradiation process. In each case, we took the number of \(\delta r\) steps as 1000. From the calculated RDF, the probability to find an atom in a shell \(dr\) at the distance \(r\) of another atom chosen as a reference point can be obtained. The mathematical expression of the RDF is

\[
g(r) = \frac{N}{V_{\text{vol}}} \frac{dn(r)}{4\pi r^2 dr}
\]

where \(dn(r)\) represents the number of atoms inside a shell region between \(r\) and \(r + dr\) for a given system. \(N\) and \(V_{\text{vol}}\)
are the total number of atoms in the model and its volume, respectively. Another reason why we calculated the RDF is that the internal energy of the system is related to the pair correlation function.

The RDFs at room temperature were calculated first and the results are shown in figure 4. It can be clearly seen that there are peaks and valleys distributing in the range of $0 - 7\,\text{Å}$, which reflect the regular arrangement of germanium atoms in the crystal at room temperature. In order to obtain the structural information of germanium under irradiations of difference femtosecond laser fluences, we chose the cases with electron temperatures of 20 000 K, 30 000 K and 60 000 K to calculate the RDFs for comparison (see figures 5–7). The temporarily stable ion temperatures for the three cases are approximately 400 K, 1500 K and 3500 K, respectively. We also computed the RDFs for germanium in three phases (corresponding to 400 K, 1500 K and 3500 K) and the electron temperature and ion temperature are equal (see the purple curves in figures 5–7).
Figure 6. RDFs at different stages, liquid state (30,000 K).

Figure 7. RDFs at different stages, gas phase (60,000 K).

Figure 8. MSD of germanium crystal at room temperature.

For the case of electron temperature 20,000 K, comparing the red curve with the green and blue curves, we can see that even though the ion temperature does not rise to the melting point by the hot electrons, the structure has already changed. As seen in figure 1, the temporarily stable temperature of the case of 20,000 K is around 400 K. Thus, to make the prediction even more persuasive, we calculated the RDF of germanium, whose temperatures of electronic subsystem and the ionic subsystem are both set as 400 K (see the purple curve in figure 5). The profile of the purple curve in figure 5 resembles the curve in figure 4, which indicates atoms in the solid germanium are kept as ordered arrangements. In addition, we compare the purple curve and the red curve, because the ion temperatures are approximately equal and the irradiation initially starts, and the RDF results show the almost overlapping profiles.

3.4. Thermal motion of atoms

To quantitatively measure the extent of spatial random motion of the atoms, we calculated the mean square displacement (MSD) of the atomic thermal motion for germanium at different phases with selected stages like in section 3.3. The trajectories caused by random collisions of atoms from each other are very complex during the evolution of an MD simulation process. By adding the square of the distances, the MSD method overcomes the drawback of elimination effects induced by the addition of the positive and negative values counting from a prefixed position. The MSD is mathematically defined by taking the average of the summations of square distance:

$$\text{MSD}(t) = \langle r^2(t) \rangle = \langle |r_i(t) - r_i(0)|^2 \rangle$$  \hspace{1cm} (14)

where $r_i(t)$ represents the position of the atom $i$ at the time $t$ and $\langle \ldots \rangle$ denoted as an average on the time steps and the particles. Figure 8 shows the calculated MSD of the solid state germanium and the value at the end of the 1000 time steps (96,755 fs) is about 0.02 Å$^2$. Because the thermal motion of atoms is only characterized by phonon vibrations, there is no appreciable MSD. In figures 9–11, the calculated MSDs of different simulation stages since the femtosecond laser irradiation are plotted. A general
tendency of increasing values at the ending point of each 1000 time steps is revealed in figures 9–11. According to [10], the differences of MSDs originated the transition of valence electrons into the conduction band and the instability of transverse acoustic phonons and longitudinal optical phonons. In addition, for the cases of higher electron temperature, the MSD values are correspondingly higher. The discrepancies of purple curves between the other three curves verify the predication that germanium with equal electron temperature and ion temperature is different from the ones in which the electrons are excited. Moreover, the slope of the red curve in figure 9 is relatively steeper than the purple curve in figure 9. Thus, we can see that the motion property of the laser irradiated germanium is more like a fluid than the germanium with the same temperature at the solid state. The remarkable MSD under high energy femtosecond laser irradiation is also reported for vitreous silica [30], whose ion temperature is $\sim 500 \text{ K}$ under high energy femtosecond laser irradiation of $T_e = 25 000 \text{ K}$. In addition, other simulation results using a self-developed code for high excited valence electron system (CHIVES) [37] were reported to have quantitatively comparable MSDs of silicon under femtosecond laser excitation [16]. Another point that deserves our attention is the red curves in each of figures 9–11 when they are compared with the green and blue curves. We can find that in figure 9, the final value of the red curve MSD is 0.058 Å². However, the squared distance of thermal motion of the blue one in figure 9 (0.130 Å²) is more than 2.241 times of that in red. In addition, the ratio of the final value between blue cure and green curve gradually narrow down from figures 9 to 11. In figure 11, the blue and green curves almost coincide with each other, which indicates that the nonthermal melting of laser irradiated germanium thoroughly developed in the 2001–3000 time steps and there are no significant differences distinguishing the subsequent 3001–4000 time steps. In figure 9, the red curve of initial electronic excitation is above the purple curves with equal electron and ion temperatures. However, it differentiates from the cases in figures 10 and 11, which could be attributed to a retarded response to lower femtosecond laser fluence.

### 3.5. Dynamic property of the velocity autocorrelation function

The velocity autocorrelation function (VAF) is also an important parameter to characterize the dynamic properties of femtosecond irradiated germanium. It is important in revealing the underlying nature of the dynamic process operating in the simulated molecular system. The VAF is mathematically defined as

$$Z(t) = \frac{\sum_{i=1}^{N} (V_i(t) \cdot V_i(0))}{\sum_{i=1}^{N} (V_i(0) \cdot V_i(0))},$$

where $V_i(t)$ includes the three components of the velocity $v_x(t), v_y(t)$ and $v_z(t)$. We computed the VAFs for the system with electron temperature at 300 K, 20 000 K, 30 000 K and 60 000 K, respectively. The sampling time period is 1000 time steps for all cases. As is seen in figure 12, the computed VAFs for the last three cases are always positive, which lead to the high values of the diffusion coefficient. However, the VAF at room temperature contains both a positive part and a negative part. The results can be interpreted in terms of the thermophysical interaction of atoms. Firstly, let us consider a single atom at time zero that has a specific velocity $v,$
By assuming that the atoms in the system do not interact with each other, according to Newton’s second law, the atom will retain the initial velocity all the time; the VAF profile will be a horizontal line with the evolution of time. If the forces are small but not negligible, then the magnitude of VAF will change gradually under the influence of the weak forces. Observing the green, blue and purple lines of the 20,000 K, 30,000 K and 60,000 K cases, one can see that the VAFs render simple decays, which demonstrates that the presence of weak force slowly destroys the velocity correlations. For the solid germanium at room temperature, the atoms are compacted closely together. They will search for the position at which there is a balance between the attractive and repulsive forces and the energies of the atoms can be regarded as stable for such a system. The motion of atoms is like dots connected by springs with back and forth oscillations; so the regular position cannot be broken down and disordered. Hence, the calculated VAF shows strong oscillations from positive to negative values with periodicity. The red plot in figure 12 shows a damped harmonic motion, which verifies that the germanium at room temperature is a usual solid without excited electrons. But for the cases of 20,000 K and 30,000 K germanium after femtosecond laser irradiation, they show the resemble shapes as the 60,000 K germanium. It is contradictory to the definition of phase based on the temperature, but such contradictions prove the validity of discrepancies of germanium between $T_e\&I = 400$ K and $T_I = 400$ K. It is speculated that such 20,000 K and 30,000 K germanium states are meta-states that differentiate from the usual solid and liquid in nature. In addition, we can find that the curve of 60,000 K is the steepest among the three. The most damped curve can be considered as where there is only one collision between two atoms and then they diffuse away, which reflects the chemically covalence bond break due the exited electrons.

### 3.6. Vibrational density of state

The vibrational density of state (VDOS) can be used to characterize the number of states per interval of energy at each energy level. We calculated the VDOS by performing a Fourier transform of the VAF over all atoms. The normalized VDOS of $N$ atoms system is given by

$$g(\nu) = \int_{-\infty}^{+\infty} \sum_{i=1}^{N} (V_i(t) \cdot V_i(0)) e^{2\pi i \nu t} dt.$$  \hspace{1cm} (16)

Thermal properties, such as the heat capacity and thermal conductivity, as well as some other material properties are strongly impacted by the VDOS. Hence, to get a profound grasp of the laws governing the vibrational properties of femtosecond laser irradiated germanium is of high technological and fundamental interest. Figure 13 indicates that there are high diffusive modes in the low frequency regions. However, for the case of germanium with $T_e\&I = 300$ K at room temperature, one peak evidently distinguishes from the other three. Therefore, we can conclude that the VDOSs of the cases have changed due to the phase transitions induced by the incident femtosecond laser.

### 4. Conclusions

An ab initio molecular dynamics study of the thermal and dynamic effect induced by femtosecond laser irradiation is performed in this paper. By employing the finite temperature density functional theory and incorporating direct energy minimization, an accurate pseudopotential description of core electrons and the Nosé-Hoover dynamics temperature control of the electronic and ionic subsystem, our simulation successfully obtained the results of the germanium in three phases (solid, liquid and gas). Even though the simulation in the present work is simplified to some extent, we believe that it captures the essential melting and dynamic features induced by different thermal excitation of the electronic subsystems. The unmelted germanium shows essentially liquid and gas characteristics that are different from the usual solid germanium without excited electrons around the nucleus. The structural changes and maximum value of the atomic thermal motion depend on the excited levels of the thermalized electrons. The melting and dynamic response of the ionic system also depend on the incident laser intensity, which means the higher excited electronics subsystem, the faster
temperature response of the ionic subsystem. However, there are some thresholds for the energy of the electronic subsystem that limit the phase change from solid to liquid and liquid to gas. The melting and evaporation are determined by both the electronic and ionic sub systems. 

Our work demonstrates the great potential of \textit{ab initio} MD simulation of the femtosecond laser interaction with semiconductor materials. With the advantages over classical MD simulations where interatomic potential empirically is defined and other numerical modelling and simulation methodologies, it is possible to broaden the \textit{ab initio} MD simulation to thermodynamical problems involving the participation of electron interaction and transport in the future.

\textbf{Acknowledgment}

Support for this work by the US National Science Foundation under grant number CBET- 1066917 is gratefully acknowledged.

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