Laser-induced melting of silicon: A tight-binding molecular dynamics simulation

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The tight-binding molecular dynamics method with hot electrons is used to simulate the laser-induced melting of silicon. The results are in good agreement with previous *ab initio* simulation and experimental data. Our findings assess the reliability of the tight-binding model to describe silicon with a high concentration of excited electrons. The role of volume changes in the laser-induced melting has also been addressed within constant-pressure tight-binding molecular dynamics.

Since the discovery of laser annealing of crystal damage in ion-implanted semiconductors,[1] the study of the transformations induced by laser irradiation has acquired both technological and fundamental interest. The processes involved in laser-induced transformations depend on the characteristics of the laser pulses, such as duration, intensity, and wavelength. In particular, the duration of the pulses plays an important role: when the pulse lasts much longer than the electron-lattice relaxation time (1 ps), direct transfer of energy from excited electrons to the lattice leads to ordinary thermal melting, which occurs in a few hundreds of picoseconds after irradiation.[2] Conversely, very short laser pulses ($\sim$100 fs long and intensity of the order of TW/cm^2) promote a large fraction of valence electrons into the conduction band long before energy can be transferred to the ions via electron-lattice relaxation. This situation has been described by the plasma annealing (PA) model[3] which assumes that the transition from bonding to antibonding states of a large fraction of the valence electrons ($\simeq$10%) induces a weakening of the covalent bonds, leading to melting in a subpicosecond time scale, long before the system has time to become vibrationally excited. This process, named nonthermal melting, has been observed by means of time-resolved optical spectroscopy in several semiconductors [Si,[4–6] GaAs,[7,8] and InSb (Ref. 9)] irradiated with ultrashort (60–100 fs) laser pulses.

Molecular dynamics (MD) simulations can help in elucidating the microscopic details of laser-induced transformations. An *ab initio* method based on finite-temperature density functional theory[10] has been recently used to study the nonthermal melting of silicon.[11] This method, which incorporates self-consistently the effects of the electronic excitation, is suitable to describe the system after irradiation with very short laser pulses. In fact, since the electron-electron relaxation time ($\sim$10 fs) is much shorter than the electron-lattice relaxation time (1 ps), the electrons can be considered, as a first approximation, in internal equilibrium at a constant temperature T_{el} for about 1 ps after irradiation. The electronic temperature T_{el} is different from the ionic temperature and is controlled by the energy absorbed from the laser pulse. The ions are instead free to evolve under the action of the interatomic forces strongly modified by the high fraction of excited electrons. Reasonable estimates show that T_{el} can reach values of order of 10^4 K for typical experimental laser fluences.[6] *Ab initio* calculations have shown that at sufficiently high excitation, crystalline silicon transforms in about 150 fs into a fluid phase (hereafter referred to as l′-Si) with properties different from ordinary liquid silicon (at $T_{el} = T_{ion} \simeq 1680$ K).[11]

In recent years, tight-binding molecular dynamics (TBMD) has proven to have good overall reliability in describing the properties of silicon with cold electrons.[14] In this paper we investigate the possibility of extending the field of applicability of TBMD to those phenomena involving high electronic excitations such as laser-induced melting. Recently, a similar study of laser-induced fragmentation of small silicon clusters based on TBMD has been published.[12] However, the lack of experimental data on small silicon clusters to directly compare with did not allow full assessment of the reliability of the TB model to describe electronically excited silicon. For this purpose we have chosen to simulate the laser-induced melting of silicon, since the availability of detailed *ab initio* data on this process allows for a thorough comparison. We find that the TB description of the nonthermal process and of the properties of the hot-electron liquid is in very good agreement with the *ab initio* results. This outcome encouraged us to enlarge the scope of the present work and to address also the role of volume changes in nonthermal melting by performing constant-pressure TBMD simulations. It turns out that the high electronic excitation driving the nonthermal melting also induces a volume expansion of 20%, as opposed to the 9.5% volume contraction at the ordinary solid-liquid transition in silicon.[13] Nevertheless, all the main features of the transformation process and the properties of the final phase are very similar to the outcome of constant-volume simulations. Therefore our results represent also a validation of the main conclusions of the previous *ab initio* work[11] where volume changes were neglected.

In order to check the transferability of the TB model we first included the effects of electronic excitations in the same way used in the previous *ab initio* work.[10] The Fermi-Dirac

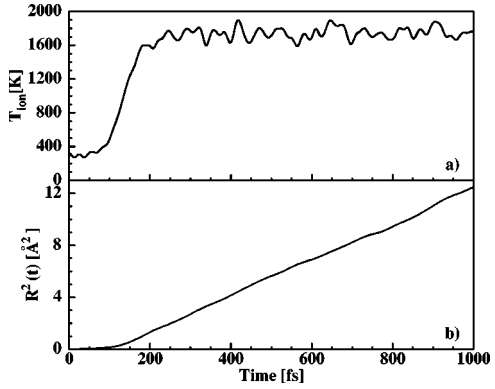

FIG. 1. (a) Instantaneous ionic temperature and (b) atomic mean square displacement as a function of time after irradiation.

distribution of the occupation of the electronic states at finite temperature has been implemented in TBMD as discussed in Refs. 15,12. We used TBMD with an orthogonal sp^3 Hamiltonian which is known to reproduce the thermal melting of Si and the structural properties of ordinary liquid Si (l-Si, hereafter).[14,16] The effect of the irradiation with very short laser pulses is simulated by suddenly increasing T_{el} which is then held fixed during the simulation as in the *ab initio* scheme of Refs. 10,11. On the ps time scale, hot-carrier diffusion[8] is the most important source of energy leakage leading to a decrease of T_{el}. As a first approximation, the latter effect has been neglected in the *ab initio* simulations of Ref. 11 and in our simulation as well in order to exactly reproduce the *ab initio* results. As discussed later on, the parameter T_{el} can be directly related to the laser fluence in the experimental setup.

We performed constant-volume MD runs at the experimental density of 2.33 g/cm^3 and at several T_{el} in the range 10 000–25 000 K. We first used a simple cubic supercell containing 64 Si atoms with periodic boundary conditions. Only the supercell Γ point was used in the Brillouin zone sampling. We then repeated some of the simulations with a 216-atom cubic supercell without observing any relevant size effect. We here report the results obtained with the 216-atom samples. The adopted simulation strategy is as follows: we first equilibrated the sample for 2 ps at $T_{ion}=300$ K with electrons and ions in thermal equilibrium; then we suddenly increased T_{el} and the ions were allowed to evolve freely at constant T_{el}.

Two different regimes are observed: for $T_{el}\leqslant 14\,000$ K the system does not undergo a melting transition, while for higher T_{el} the transition occurs in a few hundreds of femtoseconds. For $T_{el}\leqslant 10\,000$ K the ions perform oscillations around their equilibrium positions slightly wider than the room temperature motion. At $T_{el}=14\,000$ K a slight distortion was observed but the system does not melt on the simulation time scale (1 ps).

The situation is remarkably different at $T_{el}=18\,000$ K, when the fraction of excited electrons[21] is about 10% of the valence electrons. About 100 fs after irradiation the ionic temperature (T_{ion}) begins to increase and the system transforms into a disordered phase in about 200 fs; the ionic temperature T_{ion} fluctuates around 1750 K, which is close to the experimental melting point of Si ($T_m=1680$ K) [see Fig. 1(a)]. The system is liquid as shown by the linear increase of

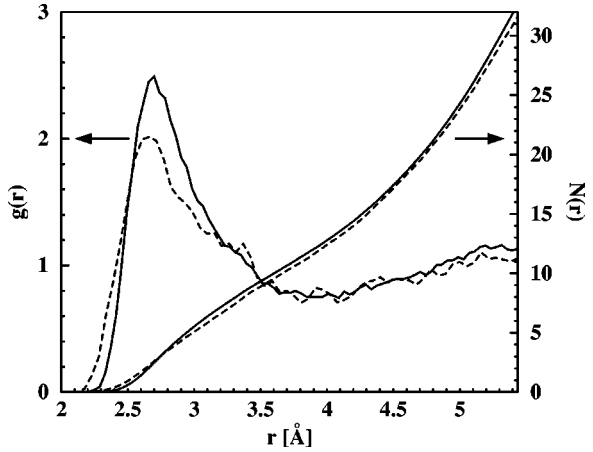

FIG. 2. Pair correlation function $g(r)$ and coordination number $N(r)$ of l′-Si. Solid lines represent the TBMD results at $T_{el}=18\,000$ K. Dashed lines are the *ab initio* results at $T_{el}=25\,000$ K.[11]

the mean square displacement in Fig. 1(b) and the calculated self-diffusion coefficient $D=2.5\times10^{-4}$ cm^2/s. The behavior of the system at $T_{el}=18\,000$ K is very similar to that observed in the *ab initio* simulations at $T_{el}=25\,000$ K, showing a fast transition ($\sim$150 fs) to a liquid state with ionic temperature $T_{ion}\sim1700$ K and self-diffusion coefficient of 2.7 $\times10^{-4}$ cm^2/s.[11] The structural properties of the hot-electron liquid (l′-Si) found in the *ab initio* simulation are quite well reproduced by our calculation, as shown by the comparison of *ab initio* and TBMD pair correlation functions $g(r)$ in Fig. 2. By integrating $g(r)$ up to the first minimum (4.0 Å) we find a coordination number of 12.5, close to the *ab initio value* (11–13).

The structural properties of l′-Si are different from those of l-Si as shown by the comparison of their pair correlation functions in Fig. 3. The electronic excitation induces a broadening and a shift of the first peak of the $g(r)$ from 2.56 Å in l-Si to 2.70 Å in l′-Si. The calculated coordination number is also much larger in l′-Si (13) than in ordinary l-Si

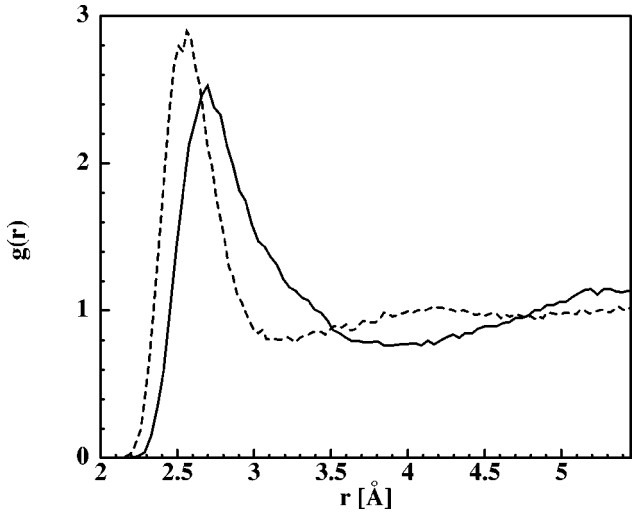

FIG. 3. Pair correlation function of l′-Si at $T_{el}=18\,000$ K and $T_{ion}=1750$ K (solid line) and of the ordinary liquid silicon at $T_{el}=T_{ion}=1800$ K (dashed line) equilibrated within TBMD.

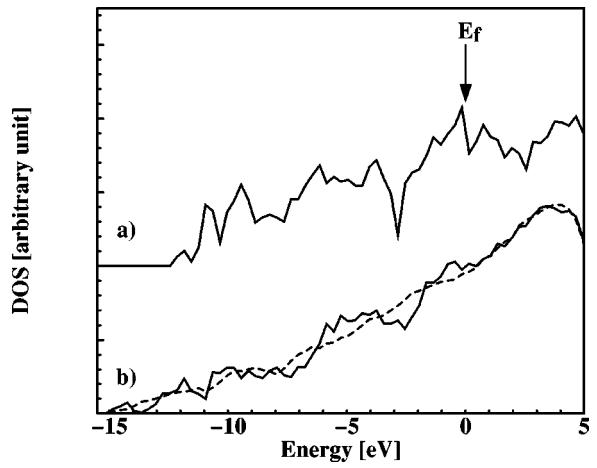

FIG. 4. Electronic density of states (DOS) for l′-Si: (a) *ab initio* calculation at $T_{el}=25\,000$ K in a 64-atom sample; (b) TBMD calculation at $T_{el}=18\,000$ K with 64 atoms (solid line) and 216 atoms (dashed line). The DOS have been averaged over 50 ionic configurations; only the supercell Γ point has been used. The arrow indicates the position of the Fermi level.

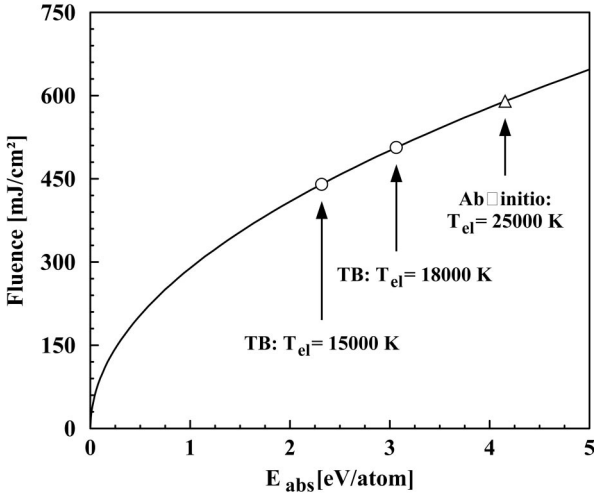

FIG. 6. Relation between E_{abs} and the laser fluence F calculated for typical fs laser pulses (see text). The open circles represent the value of E_{abs} and F corresponding to two runs at different T_{el} within the TB framework while the open triangle corresponds to the *ab initio* simulation at $T_{el}=25\,000$ K (Ref. 11).

(6.5). As reported in the previous *ab initio* simulation, we verified that by instantaneously decreasing the electronic temperature to the ionic temperature (1750 K), l′-Si reverts to ordinary l-Si with an increase of ionic temperature up to 2100 K. Calculation of the electronic density of states reveals that l′-Si is metallic, in agreement with the *ab initio* result (see Fig. 4).

At higher T_{el}, the ionic temperature is higher ($T_{ion}\sim 3500$ K at $T_{el}=25\,000$ K), but the structural and electronic properties of the fluid phase are close to those of l′-Si above the threshold temperature for laser-induced melting ($T_{el}=18\,000$ K).

We can make contact with the experimental data by estimating the laser fluence corresponding to the different electronic temperatures used in the simulation. In fact, T_{el} can be directly related to the laser fluence by equating the total energy absorbed by the system in the simulation and in the experiments. In the simulation an instantaneous energy absorption is due to the initial sudden increase of T_{el}. A second energy transfer occurs when the system transforms at constant T_{el}. The latter energy absorption lasts for the duration of the transformation process, i.e., less than 150 fs, a time scale comparable with the duration of the laser pulse. Therefore, for $T_{el}<15\,000$ K, when no transformation occurs, the simulation describes only an instantaneous energy absorption at the beginning of the run, while for $T_{el}>15\,000$ K it mimics a continuous energy absorption lasting for the time scale of the typical ultrashort laser pulses (100–200 fs). The total absorbed energy (E_{abs}) as a function of T_{el} is shown in Fig. 5. The discontinuity corresponds to the onset of nonthermal melting. The additional increase in E_{abs} occurring during the transformation is given by $T_{el}\Delta S_{el}$, where ΔS_{el} represents the change in the electronic entropy across the transformation at constant T_{el}.

On the other hand, E_{abs} can be expressed as a function of the fluence, pulse duration, and absorption coefficients of the sample. At the intensities generally used in femtosecond laser experiments (TW/cm^2) the absorption is due both to lin-

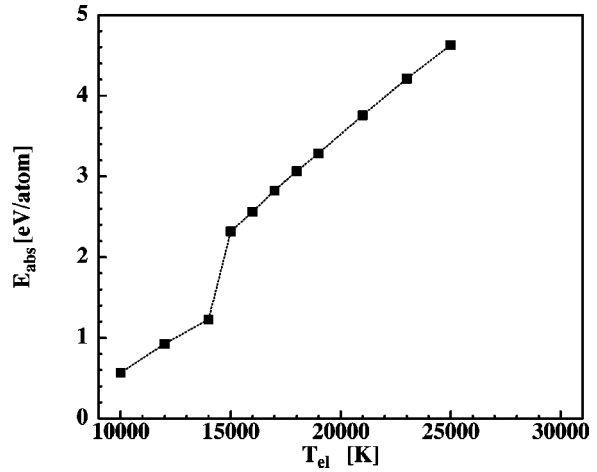

FIG. 5. Relation between T_{el} and E_{abs} in the tight-binding simulations.

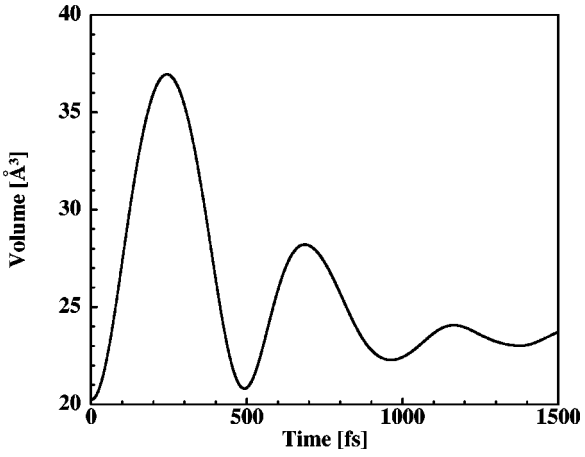

FIG. 7. Volume of the simulation cell as a function of time after irradiation in the constant-pressure simulation at $T_{el}=18\,000$ K.

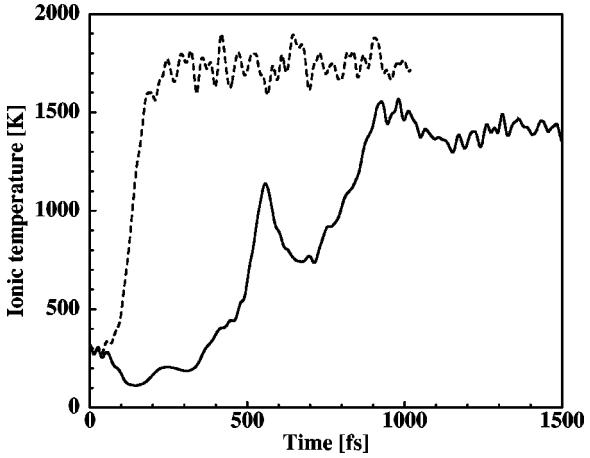

FIG. 8. Instantaneous ionic temperature as a function of time after irradiation in the constant-pressure (solid line) and constant-volume (dashed line) simulations.

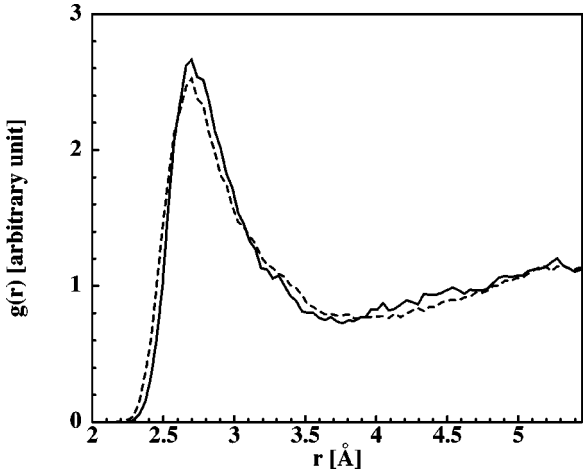

FIG. 9. Pair correlation function $g(r)$ of l′-Si obtained in the constant-pressure (solid line) and constant-volume (dashed line) simulations.

ear (one-photon absorption) and nonlinear (two-photon absorption) processes. Consequently the decrease of intensity I of the laser pulse as a function of the penetration depth z into the sample is given by

$$\frac{dI}{dz} = -\alpha I - \beta I^2, \tag{1}$$

where α and β are, respectively, the one-photon and two-photon absorption coefficients. The experimental absorption coefficients at high intensities ($I_0 \sim 0.1$–1 TW/cm^2) are $\alpha \simeq 3500$ cm^{-1} and $\beta \simeq 40$ cm/GW.[6] For femtosecond laser pulses and fluence of the order of 10–100 mJ/cm^2 the one-photon contribution is negligible. Therefore, by assuming that the laser energy is absorbed in a volume of thickness $\tilde{z}$ such that $I(\tilde{z}) = I_0/e$ (e is the Neper number) the absorbed energy E_{abs} is given by

$$E_{abs} = (1-R)\frac{\beta F^2}{n \tau_p e}, \tag{2}$$

where R is the reflectivity (~ 0.35, Ref. 17), τ_p the pulse duration (100 fs for instance) and n the atom density of silicon (4.997×10^{22} atoms/cm^3). The fluence corresponding to the threshold electronic temperature ($T_{el} = 15\,000$ K) for nonthermal melting is ~ 440 mJ/cm^2 (see Fig. 6) which is close to the experimental value (350–500 mJ/cm^2, Ref. 6). The penetration depth in these conditions is $\tilde{z} \sim 1000$ Å . The threshold electronic temperature in the *ab initio* simulation corresponds instead to a fluence of 590 mJ/cm^2, as computed from the *ab initio* absorbed energy (Fig. 6).

In order to check how the rate of energy absorption from the laser could change the transformation process, we have also performed another simulation by fixing the occupation numbers of the single-particle states instead of fixing T_{el}. In this case the energy absorption occurs only when the initial T_{el} is suddenly raised. We can choose the initial T_{el} in a simulation at constant occupation number in such a way that the energy absorbed equals the energy absorbed in the simulation at constant $T_{el} = 18\,000$ K. It turns out that whenever the total energies absorbed in the simulations at constant T_{el} and at constant occupation number are the same, the two simulation schemes produce the same l′-Si phase and very similar transformation dynamics. This result implies that the final configuration after a few hundreds of femtoseconds is not strongly dependent on the way the energy is absorbed in the regimes considered here.

So far, we have assumed that the constraint of fixed density imposed in the constant-volume simulations has no dramatic effect on the nonthermal melting process. In order to check the validity of this assumption we have performed constant-pressure[18,19] TBMD simulation with hot electrons at the same electronic temperatures as the constant-volume simulations reported above. Above the threshold for nonthermal melting ($T_{el} = 18\,000$ K) the electronic excitation induces a pressure increase up to 13.5 GPa. In the constant-volume simulation the pressure decreases rapidly and stabilizes around 4 GPa in the l′-Si phase. In the constant-pressure simulation the initial pressure shock provokes large fluctuations in volume which dumps down in about 1.5 ps (see Fig. 7). The final specific volume in l′-Si is 20% larger than the initial value, as opposed to the 9.5% volume shrinkage at the ordinary solid-liquid transition in silicon.[13] A fraction of the energy transferred by the laser to the electrons is transformed into mechanical work during the expansion. As a consequence, the final ionic temperature of l′-Si is somehow lower (~ 1300 K) than the temperature reached in the constant-volume simulation (see Fig. 8). The large volume fluctuations and the longer time needed to stabilize the ionic temperature in the constant-pressure simulation are due to the small size of the supercell used. Despite the large volume change, the structure of the l′-Si phase in constant-pressure and constant-volume simulations is very similar, as shown by the comparison of their $g(r)$ in Fig. 9. However, the dynamics of the expansion process in Fig. 7 is not a realistic description of the experimental situation. The very fast expansion seen in the simulation is an artifact of the small size of the simulation cell. In reality the hot spot is embedded in a cold matrix with a different compressibility and the time scale for the expansion is given by the time needed for a sound wave to cross the hot spot. Nevertheless, the outcome of the constant-pressure simulation is valuable since the latter situation corresponds to the other extreme from the

constant-volume approximation. The similarities between the l′-Si phases in the constant-volume and in the constant-pressure runs confirm that both approximations do not severely compromise the qualitative description of the transformation process. The structure of the expanded l′-Si phase is not dependent on the cell size as checked by comparing the results of simulations with 64 and 216 atoms. Conversely, at higher electronic excitations striking differences emerge between constant-volume and constant-pressure simulations. For instance, in a constant-volume simulation at $T_{el} = 25\,000$ K the ionic temperature fluctuates around 3500 K, very close to the vaporization temperature of silicon (3545 K, Ref. 20), while in the constant-pressure simulation the system vaporizes, expanding indefinitely. Therefore, the electronic excitation in this latter case is above the threshold for laser ablation.

In conclusion, we have shown that, although less accurate than the *ab initio* framework, the TB model seems to capture the most important features of the nonthermal melting of silicon. Our description of the nonthermal melting process and of the properties of the l′-Si phase is in agreement with the *ab initio* results but for the fact that in TBMD the nonthermal melting occurs at a level of electronic excitation somehow lower than in the *ab initio* simulations. However, the calculated threshold fluences of *ab initio* and TB models are both within the experimental uncertainties. The success of TBMD allowed us to address the effects of volume change in the laser-induced melting within constant-pressure TBMD. Although the hot-electron liquid expands by 20% with respect to the cold solid, the main structural features of l′-Si are not very much affected by the volume expansion. This result confirms the validity of the conclusions of the previous *ab initio* simulations where volume changes have been neglected. The less computer-intensive TBMD might also address other details of the nonthermal process which are more difficult to simulate by *ab initio* methods. The role of the hot-carrier diffusion, for instance, which is probably not negligible in the 100 fs time scale,[6] could be easily included phenomenologically in a TBMD scheme as was done in a recent TB simulation of the laser-induced graphitization of diamond.[22]

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