# *Ab initio* Molecular Dynamics Simulation of Laser Melting of Silicon

Pier Luigi Silvestrelli,[1] Ali Alavi,[2] Michele Parrinello,[1] and Daan Frenkel[3]
[1]*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany*
[2]*Atomistic Simulation Group, School of Mathematics and Physics, The Queen's University, Belfast BT7 1NN, Northern Ireland, United Kingdom*
[3]*FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands*
(Received 21 May 1996)

The method of *ab initio* molecular dynamics, based on finite temperature density functional theory, is used to simulate laser heating of crystal silicon. We have found that a high concentration of excited electrons dramatically weakens the covalent bond. As a result, the system undergoes a melting transition to a metallic state. In contrast to ordinary liquid silicon, the new liquid is characterized by a high coordination number and a strong reduction of covalent bonding effects. [S0031-9007(96)01372-5]

PACS numbers: 61.20.Ja, 61.80.–x, 64.70.Dv, 65.50.+m

The phenomenon of laser-induced annealing in semiconductors has attracted, over the years, considerable attention and contradictory explanations [1,2]. One of the first attempts to explain the observed phenomenology has been the "plasma annealing" (PA) model [1]. In this model it is suggested that a tetrahedral semiconducting material, subject to intense laser irradiation, can be driven directly into a disordered state, long before the system has time to become vibrationally excited. In fact, laser irradiation induces electronic transitions from the bonding to the antibonding states, thus depleting the bond charges. A high level of electronic excitation could severely weaken the interatomic bonds so that room temperature atomic motions can lead to the disordering of the lattice. The alternative explanation [2] was that direct energy transfer between the excited electrons and the ions leads to ordinary thermal melting (TM).

For laser pulses lasting 20 ps and longer, TM appears to be [2,3] the dominant mechanism. However, for very short irradiation times ($\sim$100 fs), recent time-resolved experiments have strongly strengthened the PA model. In fact several groups [4] have observed laser-induced melting of a GaAs crystal under high laser irradiation. Tom, Aumiller, and Brito-Cruz [5] have reported a loss of cubic order in crystalline Si only 150 fs after an intense 100 fs optical pulse. Shank, Yen, and Hirlimann [6] have observed melting of silicon on a time scale of less than 1 ps after a 90 fs pump pulse, as evidenced by reflectivity and second-harmonic generation. In spite of this strong experimental evidence, a clear understanding of the processes that take place is still missing.

Since reasonable estimates [7] suggest that the relaxation time for the electrons, $\tau_{ee} \sim 10^{-14}$ sec, is much shorter than the electron-ion relaxation time, $\tau_{eI} \sim 10^{-12}$ sec, we can treat the subsystems of electrons and ions in a different way. We assume that, after irradiation and for times smaller than $\tau_{eI}$, the electron subsystem remains in internal equilibrium at the initial laser-induced temperature, which is different from that of the ions. The ions instead are allowed to evolve freely. In order to describe this situation we used the *ab initio* molecular dynamics (MD) simulation technique introduced by Alavi *et al.* [8]. This method is based on finite temperature density functional theory (DFT), and incorporates self-consistently the effects of thermal electronic excitations and fractionally occupied states. Thus it is particularly suited to describe the electronically hot subsystem. We find that, as a result of the large concentration of excited electrons, the effective ion-ion interactions are changed. This leads to the melting of the crystal and to the formation of a liquid metal with properties different from those of ordinary liquid Si ($l$-Si).

Our *ab initio* MD simulation has been performed at constant volume, by assuming the experimental density of crystalline Si at room temperature, namely, $\rho = 2.329\ \mathrm{g\,cm^{-3}}$ (Ref. [9]). We used norm-conserving pseudopotentials [10] with $s$ nonlocality only. The $\Gamma$ point only was used to sample the Brillouin zone (BZ) of the MD supercell, containing $N = 64$ atoms with periodic boundary conditions (PBC) of the simple cubic type. The electronic orbitals were expanded in plane waves with a cutoff of 9.4 Ry.

Since we have assumed that the electrons are in equilibrium at a temperature $T_{\mathrm{el}}$, their density $n(\mathbf{r})$ has to be computed by minimizing the electronic free energy $\mathcal{F}$. Following Ref. [8], we write

$$\mathcal{F} = \Omega + \mu N_e + E_{II}\,, \tag{1}$$

where

$$\Omega[n(\mathbf{r})] = -\frac{2}{\beta}\ \ln\det(1 + e^{-\beta(\mathcal{H}-\mu)}) - \int d\mathbf{r}\, n(\mathbf{r})\left(\frac{\phi(\mathbf{r})}{2} + \frac{\delta\Omega_{\mathrm{xc}}}{\delta n(\mathbf{r})}\right) + \Omega_{\mathrm{xc}}\,, \tag{2}$$

$\beta = 1/(k_B T_{\mathrm{el}})$ is the inverse electronic temperature, $\mu$ is the chemical potential, $N_e$ is the total number

  

of valence electrons, $\mathcal{H} = -(1/2)\nabla^2 + V(\mathbf{r})$ is the one electron Hamiltonian with the effective potential $V(\mathbf{r}) = \sum_I V_{eI}(\mathbf{r} - R_I) + \phi(\mathbf{r}) + \delta\Omega_{\rm xc}/\delta n(\mathbf{r})$, $\phi(\mathbf{r})$ is the Hartree potential of an electron gas of density $n(\mathbf{r})$, $\Omega_{\rm xc}$ the exchange-correlation energy [11] in the local-density approximation (LDA), and $E_{II}$ the classical Coulomb energy of the ions. $\mathcal{F}$ reproduces the exact finite-temperature density of the Mermin functional [12] and was optimized for each ionic configuration using a self-consistent diagonalization method [8]. The electronic density so computed, together with the Hellmann-Feynman theorem, enables the calculation of the ionic forces. The ionic degrees of freedom were integrated using a time step of 25 a.u. ($\sim$0.6 fs). We are well aware that LDA underestimates [13] the energy gap and, furthermore, use of the $\Gamma$ point only of the supercell gives a poor representation of the density of states of the conduction band. However, the antibonding character of the conduction states is preserved and, at high levels of excitation, only the gross features of the conduction band are relevant, and these are well described by our approximation.

In the first part of the simulation the system has been equilibrated, for 0.3 ps, at a temperature of 300 K, the Si ions being allowed to perform small oscillations around the sites of a perfect diamond lattice. In this phase the electronic temperature has been kept equal to the average ionic temperature ($T_{\rm el} = 300$ K), that is, the electrons were assumed to be in thermal equilibrium with the ions. After that the effect of laser irradiation has been simulated by suddenly increasing $T_{\rm el}$ to 25 000 K. This electronic temperature corresponds to a typical photon energy ($\sim$2.15 eV) of the laser radiation pulses used in experiments [1,5]. After irradiation we kept the electrons in this highly excited state, and we continued the MD simulation in the microcanonical ensemble. In the first 0.1 ps, the silicon ions acquired a large amount of kinetic energy due to the fact that they were subject to interactions that were quite different from the ones operative at $T_{\rm el} = 300$ K. Then the ionic temperature stabilized around a value of $\sim$1700 K, which is very close to the experimental melting point of Si (1680 K). In the following 0.3 ps, we have computed the averaged values of several structural and electronic properties of the laser-heated system.

The instantaneous value of the ionic temperature is shown in Fig. 1. It remains stable for about 60 fs, after which it rises monotonically to reach a new equilibrium value of $\sim$1700 K. At this temperature the system behavior is highly diffusive. The atomic mean-square displacement increases monotonically with an estimated diffusion coefficient comparable to that of $l$-Si [14]. Several conclusions can be drawn from this observation. The system disorders; however, the hypothesis [1,4,5] that this happens while the lattice remains relatively cold can be rejected. Furthermore, melting does not proceed via a mechanical instability due to phonon softening [1,15].

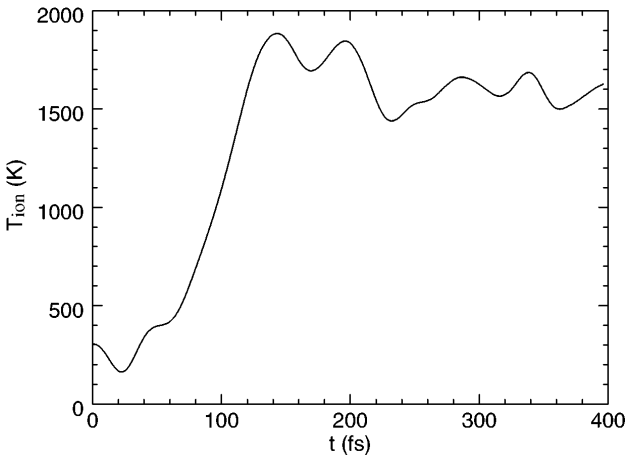


FIG. 1. Time dependence of the instantaneous ionic temperature, defined as $T_{\rm ion}(t) = [M/(3N - 3)k_B]\sum_{I=1}^{N} v_I^2(t)$, where $k_B$ is the Boltzmann constant, $M$ is the Si ion mass, and $v_I(t)$ the ionic velocity at time $t$.

In fact, after irradiation, initially the ionic instantaneous temperature decreases. We have explicitly checked that, in the diamond structure, using the free-energy functional of Eq. (1) with $T_{\rm el} = 25\,000$ K, the phonon modes are all positive, albeit somewhat softer (of the order of 10%) than in the equilibrium ($T_{\rm el} = 300$ K) Si lattice. Melting therefore proceeds via a different mechanism. Laser irradiation changes rather abruptly the interatomic potential. Thus the system finds itself in a metastable region of phase space. After about 60 fs, under the action of the new potential, it undergoes a collective transition to a new equilibrium state, which is a new liquid form of silicon ($l'$-Si), in order to lower its free energy. However, this new state of Si is only a transient. In fact, when the electrons decay to their ground state and the excess energy is dissipated, Si will revert to its usual thermodynamic behavior.

It is interesting and instructive to study the properties of $l'$-Si. Besides the already mentioned diffusion coefficient, the electronic density of states and the frequency-dependent electrical conductivity $\sigma(\omega)$, computed by the Kubo-Greenwood formula [16], appear to be (Fig. 2) very similar to those of $l$-Si [14]. Use of the Kubo-Greenwood formula in the present metastable situation (hot electrons, cold ions) is justified due to the assumption $\tau_{ee} \ll \tau_{eI}$. By extrapolating $\sigma(\omega)$ to zero frequency, we have obtained a dc electrical conductivity $\sigma \sim 17.5 \times 10^3\ \Omega^{-1}\,{\rm cm}^{-1}$ that is exactly the same value calculated in the simulation [14] of $l$-Si, and close enough to the experimental value ($12.4 \times 10^3\ \Omega^{-1}\,{\rm cm}^{-1}$) measured [17] in $l$-Si.

Rather different, however, is the pair correlation function $g(r)$ (Fig. 3) which more closely reflects the laser-induced change in the interatomic potential. Although somewhat noisy, due to the short run, the $g(r)$ clearly exhibits a remarkable shift in the position of the first peak which moves from the *ab initio* MD value of 2.4–2.5 Å

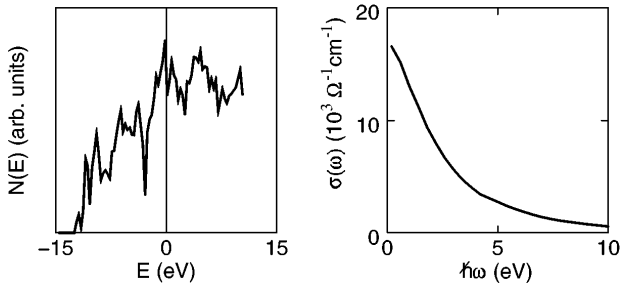


FIG. 2. Left panel: Single-particle electronic density of states $N(E)$; the vertical line indicates the position of the chemical potential $\mu$. $N(E)$ appears somewhat ragged due to the use of the $\Gamma$ point only sampling of the BZ and to the shortness of the run. Right panel: Electrical conductivity $\sigma(\omega)$ computed, averaging over 20 uncorrelated ionic configurations, the result of the Kubo-Greenwood formula [16]: $\sigma(\omega, R_I) = (2\pi e^2/3m^2\omega V_b) \sum_{i,j} (f_i - f_j) \times |\langle\psi_i|\hat{p}|\psi_j\rangle|^2 \delta(E_j - E_i - \hbar\omega)$, where $e$ and $m$ are the electronic charge and mass, $V_b$ is the simulation box volume, $\hat{p}$ is the momentum operator, and $\psi_i$, $E_i$ are the electronic DFT eigenstates and eigenvalues (with their corresponding occupation numbers $f_i$), calculated for the ionic configuration $\{R_I\}$.

[14,18] (experimental 2.40 Å [19]) for $l$-Si to a new and larger value of $\sim$2.7 Å. Furthermore, the first peak in $l'$-Si is substantially lowered and broadened. Due to an ill-defined minimum after the first peak, it is difficult to define a coordination number. We estimate it to be between 11 and 13, which is much larger than the value (6–7) of $l$-Si and approaches the high coordination of simple liquid metals. However, bonding in $l'$-Si is rather complex as reflected by the asymmetry in the first peak and the presence of a pronounced shoulder.

The dynamical properties of $l'$-Si are also strongly modified. Our computed velocity autocorrelation function (Fig. 4)

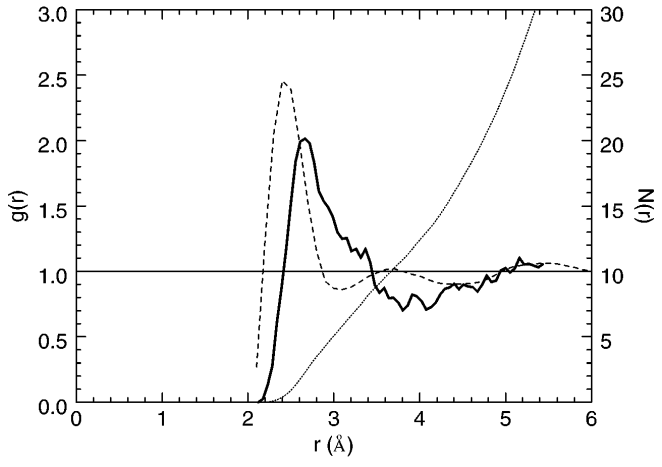


FIG. 3. Pair correlation function $g(r)$. Solid line: MD simulation. Dashed line: experimental result [19] for $l$-Si. Dotted line: coordination number $N(r)$.

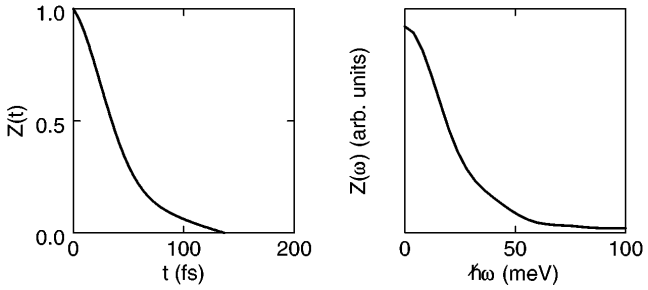


FIG. 4. Left panel: velocity autocorrelation function $Z(t)$. Right panel: the corresponding power spectrum $Z(\omega)$.

$$Z(t) = \langle \mathbf{v}(0)\mathbf{v}(t)\rangle / \langle \mathbf{v}(0)\mathbf{v}(0)\rangle \tag{3}$$

is always positive, leading to a high value of the diffusion coefficient. However, in contrast to the result of the simulation of $l$-Si [14], it does not exhibit any oscillation. Consequently, also the spectral density $Z(\omega)$, obtained by taking the Fourier transform of $Z(t)$, is quite structureless, and one cannot identify vibrational modes reflecting covalent bonding effects, as found in $l$-Si [14].

In order to clarify the effect of the high electronic temperature we have considered a fixed ionic configuration, with the ions located at the equilibrium positions of the perfect diamond lattice, and we have computed the different electronic charge distributions obtained by minimizing the free-energy functional of Eq. (1) at different electronic temperatures. Figure 5 shows contour plots of $\Delta n(\mathbf{r})$, the difference between the charge density computed at $T_{\mathrm{el}} = 25\,000$ K and that computed at $T_{\mathrm{el}} = 300$ K. As can be seen, a significant amount of electronic charge, which can be estimated of the order of 0.1 electron per atom, is removed from the covalent bond.

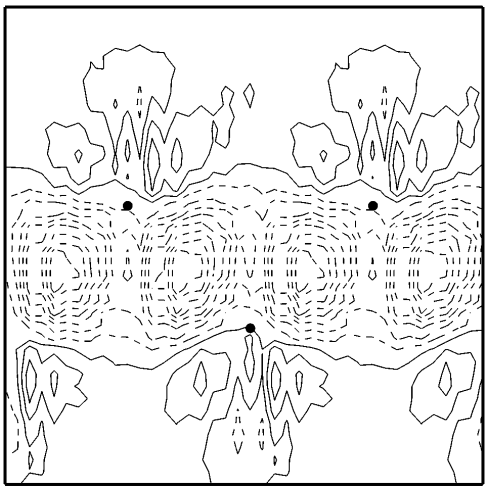

FIG. 5. Contour plots, in the (110) plane, of the difference between the electronic charge density computed at 25 000 K and that computed at 300 K. Solid (dashed) lines indicate positive (negative) density. The ions (filled circles) are located at the equilibrium positions of the perfect diamond lattice.

To give further support to the concept of weakening of the covalent bond, due to the presence of excited electrons, we have also determined the effect of the high electronic excitation ($T_{el} = 25\,000$ K) on the equilibrium structure of three simple molecules, namely, $SiH_4$, $Si_2H_6$, and $Si_2$. In $SiH_4$ the presence of the excited electrons makes the Si-H bond length significantly ($\sim 10\%$) longer. In $Si_2H_6$ the Si-H bond length is also increased considerably ($\sim 12\%$), while the Si-Si bond is completely broken. The same is true for the $Si_2$ molecule which is unstable at $T_{el} = 25\,000$ K.

We have also performed a simulation of the laser-irradiated silicon crystal in which the electronic temperature was brought to the lower value of $T_{el} = 15\,000$ K ($\sim 1.29$ eV). Under these conditions the ions oscillated wildly around their equilibrium positions but the system did not melt, at least on the time scale of the simulation ($\sim 0.4$ ps). However, since the atomic mean-square fluctuations were close to the critical value of Lindemann melting criterion, we believe that, also at this electronic temperature, one should observe melting in a long enough run. In simulations that use PBC it is not infrequent to observe superheating of a perfect crystal. This is due to finite simulation time and the absence of nucleation centers such as surfaces.

In conclusion, we have presented the results of an *ab initio* MD simulation of laser-heated Si. Admittedly, our simulation is a rather simplified modeling of the experiments. However, we think that it captures the essential features of the phenomenon. Basically, the presence of a large concentration of excited electrons changes the interatomic forces by weakening the covalent bonds of the crystal. Under the action of this modified interaction, the system melts into a metallic liquid with properties remarkably different from those of the *l*-Si. In some sense, our picture is intermediate between the PA and the TM models. As in PA, melting is triggered by the weakening of the covalent bonds; however, the temperature of the ions is increased as in TM, albeit via a mechanism rather different from that of a direct transfer of energy from electrons to ions. It would be extremely interesting if experiments could probe the properties of this new state of Si.

The work of the FOM Institute is part of the scientific program of FOM and is supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). Computer time on the CRAY-C98/4256 at SARA was made available by the Stichting Nationale Computer Faciliteiten (NCF).

[1] J. A. Van Vechten, R. Tsu, F. W. Saris, and D. Hoonhout, Phys. Lett. **74A**, 417 (1979); **74A**, 422 (1979); J. A. Van Vechten, J. Phys. (Paris), Colloq. **41**, C4-15 (1980); J. A. Van Vechten, in *Laser and Electron-Beam Interactions with Solids*, edited by B. R. Appleton and G. K. Celler (North-Holland, New York, 1981), Vol. 4.

[2] *Pulsed Laser Processing of Semiconductors*, edited by R. F. Wood, C. W. White, and R. T. Young (Academic, Orlando, 1984), Vol. 23, and references therein.

[3] *Resonances—A Volume in Honor of the 70th Birthday of Nicolaas Bloembergen*, edited by M. D. Levenson, E. Mazur, P. S. Pershan, and Y. R. Shen (World Scientific, Singapore, 1990), and references therein.

[4] S. V. Govorkov, I. L. Shumay, W. Rudolph, and T. Schroder, Opt. Lett. **16**, 1013 (1991); P. Saeta, J.-K. Wang, Y. Siegal, N. Bloembergen, and E. Mazur, Phys. Rev. Lett. **67**, 1023 (1991); K. Sokolowski-Tinten, H. Schulz, J. Bialkowski, and D. von der Linde, Appl. Phys. A **53**, 227 (1991).

[5] H. W. K. Tom, G. D. Aumiller, and C. H. Brito-Cruz, Phys. Rev. Lett. **60**, 1438 (1988).

[6] C. V. Shank, R. Yen, and C. Hirlimann, Phys. Rev. Lett. **50**, 454 (1983); **51**, 900 (1983).

[7] D. Agassi, J. Appl. Phys. **55**, 4376 (1984).

[8] A. Alavi, J. Kohanoff, M. Parrinello, and D. Frenkel, Phys. Rev. Lett. **73**, 2599 (1994).

[9] Y. Tatsumi and H. Ohsaki, in *Properties of Silicon* (INSPEC, London, 1988), p. 3.

[10] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982); L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[11] The functional $\Omega_{xc}$ is approximated by its $T_{el} = 0$ expression, since its finite-temperature corrections are negligible at the temperatures and the electronic densities of our system. See F. Perrot and M. W. C. Dharmawardana, Phys. Rev. A **30**, 2619 (1984); D. G. Kanhere, P. V. Panat, A. K. Rajagopal, and J. Callaway, Phys. Rev. A **33**, 490 (1986).

[12] N. D. Mermin, Phys. Rev. **137**, A1441 (1965).

[13] See, for instance, R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer, Berlin, 1990), p. 145, and references therein.

[14] I. Štich, R. Car, and M. Parrinello, Phys. Rev. Lett. **63**, 2240 (1989); Phys. Rev. B **44**, 4262 (1991).

[15] M. Combescot and J. Bok, Phys. Rev. Lett. **48**, 1413 (1982); R. Biswas and V. Ambegaokar, Phys. Rev. B **26**, 1980 (1982).

[16] E. N. Economou, *Green's Functions in Quantum Physics*, edited by M. Cardona, P. Fulde, and H.-J. Queisser, Springer Series in Solid State Sciences Vol. 7 (Springer, Berlin, 1983), p. 152ff.

[17] V. M. Glazov, S. N. Chizhevskaya, and N. N. Glagoleva, *Liquid Semiconductors* (Plenum, New York, 1969).

[18] I. Štich, M. Parrinello, and J. M. Holender, Phys. Rev. Lett. **76**, 2077 (1996).

[19] Y. Waseda and K. Suzuki, Z. Phys. B **20**, 339 (1975); J. P. Gabathuler and S. Steeb, Z. Naturforsch. **34A**, 1314 (1979).