Quasimomentum-Space Image for Ultrafast Melting of Silicon

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By exciting electron-hole pairs that survive for picoseconds strong femtosecond lasers may transiently influence the bonding properties of semiconductors, causing structure changes, in particular, ultrafast melting. In order to determine the energy flow during this process in silicon we performed *ab initio* molecular dynamics simulations and an analysis in quasimomentum space. We found that energy flows very differently as a function of increasing excitation density, namely, mainly through long wavelength, L-point, or X-point lattice vibrations, respectively.

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Structure changes that can be induced in solids by ultrashort laser pulses include, but are not limited to, coherent phonons [1–3], solid-solid transformations [4–7], magnetic transitions [8,9], and ultrafast melting [10–12]. For a long time, these and other phenomena could exclusively be observed through the material's time-dependent optical response, more recently, also through the time-resolved intensity of diffraction peaks after femtosecond-laser excitation [13,14]. Very recently, it has become feasible to detect the diffuse or background scattering between diffraction peaks as a function of time [15], which gives direct access to quasimomentum-dependent information [16,17]. Motivated by this experimental progress we theoretically studied the ultrafast energy transfer to and between the atomic degrees of freedom, a phenomenon not addressed so far on an atomistic level, for the example of silicon after the excitation of $n = 8.4\%$–12.8% of its valence electrons, creating as many electron-hole pairs. We found that energy does, as a rule, not predominantly flow in the direction of a laser-induced lattice instability (explained below), but follows unexpected ways; see Fig. 1.

Lots of research has been focused on unraveling the physical mechanisms of ultrafast melting of silicon, beginning four years before its discovery, when Van Vechten and co-workers, anticipating the development toward ever shorter laser-pulse excitations, published two seminal papers, respectively, giving reasons why already nanosecond pulsed laser annealing of Si does not involve simple thermal melting [18] and focusing attention on the role of the excited electron-hole pairs [19]. Two key insights in the latter publication are a phonon emission time "several orders of magnitude longer than 0.1 ps," among other reasons due to screening [20], making the electron-hole plasma equally long-lived, and a destabilization of transverse acoustic phonons or lattice instability when bond charges are depleted [21], leading to a fluid state with properties quite different from those of liquid silicon. In agreement, experimentally the electron-phonon thermalization time has been shown to increase from 0.2 to 1.2 ps when $n = 0.6\%$ of the valence electrons is excited [22] and to 2.0 ps when $n = 1.1\%$ of the valence electrons is excited [23]. In further confirmation, theoretical studies have found phonon softening [24], even of entire branches [25], and tight-binding [26] and *ab initio* molecular dynamics simulations [27,28] have quantified differences between liquid silicon and the laser-induced fluid state. Recently, we have also verified that at very high excitation density, $n = 14.1\%$, silicon melts in the directions of transverse acoustic phonons and we have indicated how this can be measured experimentally [29]. The question how the energy flows between the atomic degrees of freedom during ultrafast melting of Si is, however, still open.

In order to obtain an unbiased prediction of the complex structural response of silicon to femtosecond-laser excitation, including anharmonic effects and phonon-phonon interactions, we performed *ab initio* molecular dynamics simulations on laser-excited potential energy surfaces, which we computed on the fly using our in-house Code for Highly-excIted Valence Electron Systems [30]. Our simulation supercell, shown in Fig. 1 (top left), contains 512 atoms and is commensurable with all phonons having quasimomenta $\mathbf{q} = 0.25(n_1, n_2, n_3)$ in units of $2\pi/a$, where n_1, n_2, and n_3 are integers and a is the lattice parameter of Si. It is important to mention that this supercell thus provides on the one hand a relatively fine spacing of $\mathbf{q}$ points in quasimomentum space, while, on the other hand, it includes the high symmetry point $L = (0.5, 0.5, 0.5)$, which is important, because this is the point where a lattice instability first appears as a function of excitation density; see Fig. 4(a).

We modeled the effect of a femtosecond-laser pulse by an instantaneous raise of the electron temperature to a constant high value, assuming that (i) the laser-pulse duration is sufficiently short, (ii) the electrons thermalize

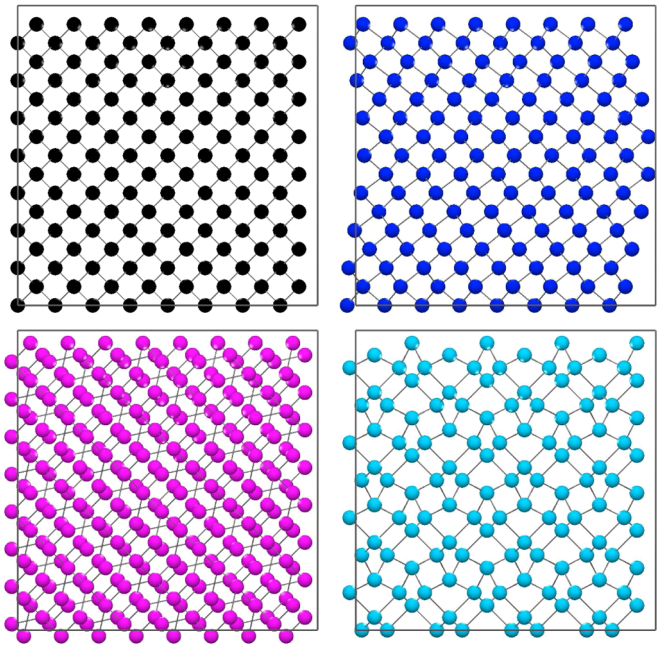

FIG. 1. 512-atom Si supercell projected in the [100] direction. (top left) Ideal atomic positions. (top right, bottom left, and bottom right) Atoms are displaced in the direction of a transverse acoustic phonon with quasimomentum $\mathbf{q} = (0.25, 0, 0)$, $\mathbf{q} = (0.5, 0.5, 0.5)$ (L), and $\mathbf{q} = (1, 0, 0)$ (X), in units of $2\pi/a$, respectively. Our present work shows that, depending on the excitation density, energy can predominantly flow into each of these phonon modes during ultrafast melting of silicon.

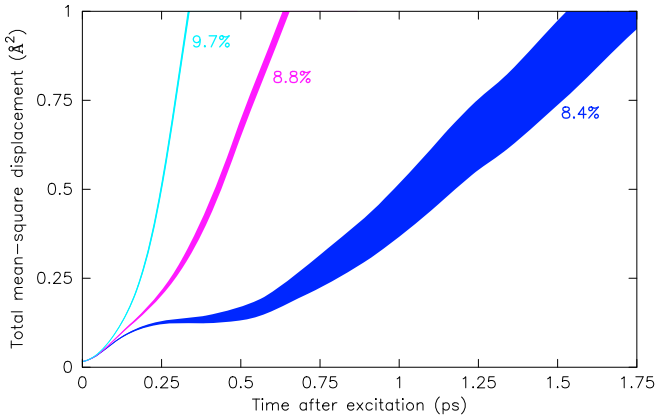

FIG. 2. Total mean-square displacement of the atoms from their ideal positions [Fig. 1(top left)] as a function of time after femtosecond-laser excitation for three electron-hole-pair densities n. The lines indicate averages over ten runs and their vertical widths equal plus and minus the standard deviations of the averages.

practically instantaneously, and (iii) the incoherent energy transfer from hot electrons to the atoms takes much longer than the typical times simulated by us. For a discussion on the validity of these assumptions we refer the interested reader to Ref. [29]. Here we would like to stress that whereas (i) characterizes the femtosecond laser, (ii) and (iii) are related to the material properties of silicon after intense laser excitation. No approximations were made with regard to anharmonicities and phonon-phonon couplings, whose relevance we establish in the present work.

For each of the electronic temperatures 0.054, 0.056, 0.058, 0.060, 0.062, 0.063, 0.064, and 0.074 Hartree/k_B with k_B the Boltzmann constant, which lie above the threshold for ultrafast melting [31] and which correspond to electron-hole-pair densities of $n = 8.4\%$, 8.8%, 9.3%, 9.7%, 10.2%, 10.4%, 10.6%, and 12.8% of all valence electrons, respectively, we performed ten molecular dynamics runs with different initial atomic conditions typical for Si close to room temperature $T_i = 0.001$ Hartree/$k_B = 316$ K (See Ref. [30]). Figure 2 shows the mean-square displacement of the atoms from their ideal coordinates [Fig. 1(top left)] as a function of time after femtosecond-laser excitation for three of our lowest excitation densities. It can be seen that the atoms move irreversibly away from their crystalline positions within hundreds of femtoseconds, in other words, silicon melts ultrafast. We stopped our simulations when the mean-square displacement reached 1 Å^2.

Figures 3(a)–3(c) show silicon's melting ways after excitation of 8.4% of the valence electrons projected on the quasimomenta along the high symmetry directions Δ, which runs from $\Gamma = (0, 0, 0)$ to $X = (1, 0, 0)$, Σ, which runs from Γ to $K = (0.75, 0.75, 0)$, and Λ, which runs from Γ to L. The projections were performed using phonon polarization vectors, see Ref. [30], where we used the fact that the subspace spanned by vectors with common $\mathbf{q}$ is invariant under laser excitation, in other words, the projections on $\mathbf{q}$ are independent of the electronic temperature. We also computed the contributions away from the high symmetry lines, but found that they were not conspicuous. In Figs. 3(a)–3(c) we see that, in each direction, the smallest quasimomentum dominates and among the directions shown the $\mathbf{q}$ vector (0.25,0,0) has the largest partial mean-square displacement. Figure 1 (top right) visualizes a typical transverse acoustic phonon with this quasimomentum, which has a long wavelength. We conclude that at low excitation density, $n = 8.4\%$, silicon melts predominantly in this and symmetry equivalent directions.

Reference [30] has predicted that laser-induced melting is precursed by thermal phonon squeezing as a function of laser fluence and, in particular, that the atomic trajectories followed are initially similar. In the latter process the atomic mean-square displacement increases, like during melting, but reversibly. Our present finding, that Si melts through a long wavelength phonon at an excitation density just above the threshold for ultrafast melting is consistent with the result in Ref. [30] that phonons with low frequencies show particularly strong squeezing. In further agreement, in germanium, which is isostructural with silicon, thermal phonon squeezing has been directly observed in a quasimomentum- and time-resolved diffuse

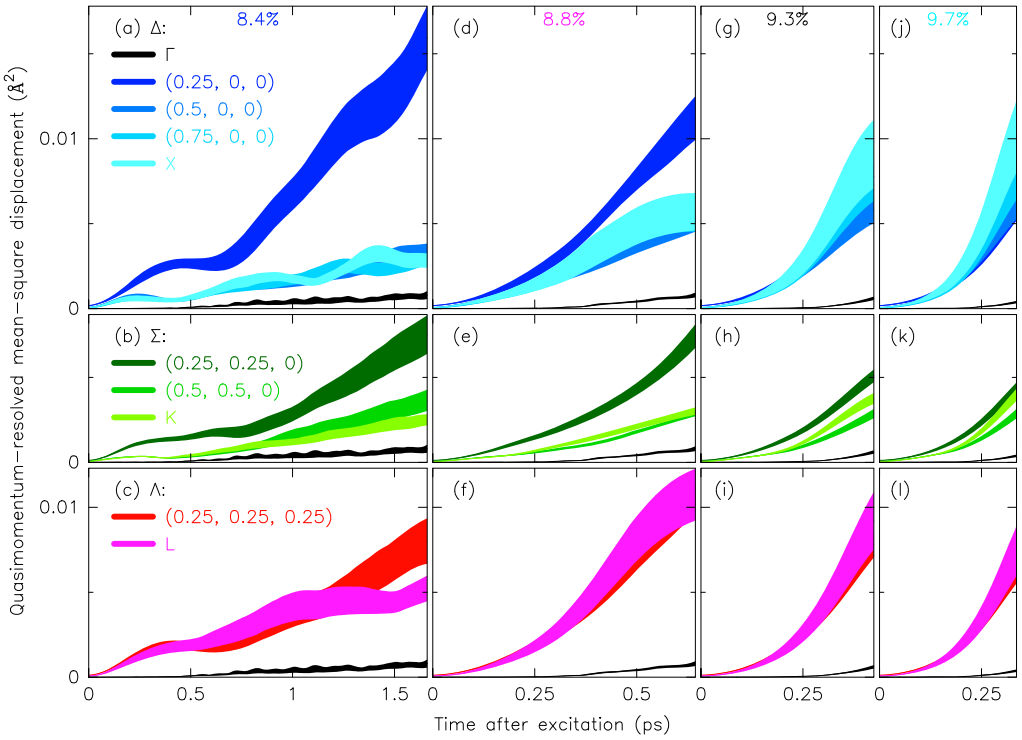

FIG. 3. Quasimomentum-resolved atomic mean-square displacement as a function of time after femtosecond-laser excitation for four electron-hole-pair densities n. Note that (a)–(c) were plotted using a different time scale than the other subfigures.

scattering experiment and the signal has been found to be strongest near the Γ point [17].

Results for higher electron-hole-pair densities n are shown in Figs. 3(d)–3(l). For $n = 8.8\%$ we see that small quasimomenta become relatively less important and that the relevance of the L point increases. Given this trend we believe that the L point contribution probably dominates in a small range of excitation densities somewhere between 8.8% and 9.3%. A typical transverse acoustic phonon with quasimomentum L is depicted in Fig. 1 (bottom left). The overall impression, however, is that the melting starts to occur throughout quasimomentum space, following many roughly equally important ways. For $n = 9.3\%$ and even more so for 9.7% the main contribution originates at the X point. At higher excitation densities we found the same qualitative behavior as in Figs. 3(j)–3(l).

It is important to remark that silicon has no lattice instability at the excitation densities visualized in Fig. 3 [32]; i.e., all phonon modes have real frequencies and the potential energy surface is attractive everywhere in the close vicinity of the ideal silicon crystal structure [Fig. 1 (top left)]. Therefore, our finding that, depending on the excitation density, silicon melts in the direction of a long wavelength, an L-, or an X-point phonon is surprising and could not have been obtained by analyzing lattice instabilities. This becomes even clearer when we consider our lowest laser excitation that produces an instability, namely, $n = 10.6\%$. For this case we plotted the phonon band structure in Fig. 4(a). Analysis shows that the L point is the only quasimomentum commensurable with our supercell that becomes unstable. Figure 4(b) shows the quasimomentum-resolved mean-square atomic displacement as a function of time after femtosecond-laser excitation for the

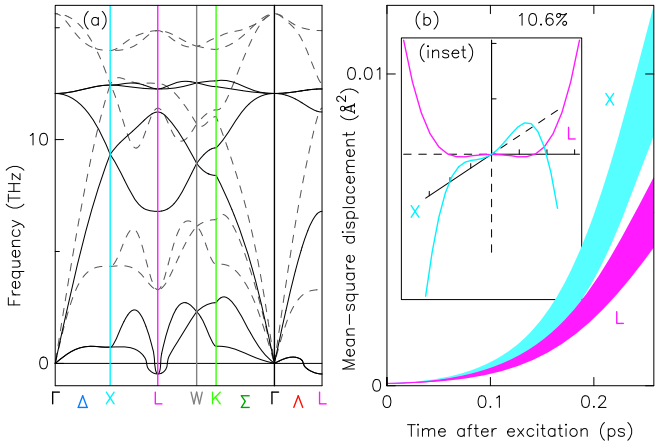

FIG. 4. (a) Phonon band structure (dashed) before and (solid lines) after femtosecond-laser excitation, $n = 10.6\%$. Imaginary frequencies are shown as negative values. (b) Average mean-square displacement of the atoms from their ideal positions in the points X and L. (inset) Potential energy surface for atomic displacements in the direction of transverse acoustic phonons with quasimomenta X and L; see Fig. 1. Tick marks indicate (x and y axes) 0.1 Å and (z axis) 0.1 eV.

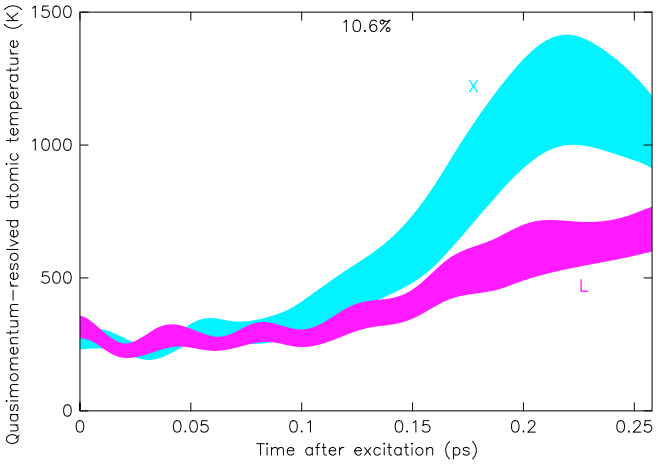

FIG. 5. Quasimomentum-resolved atomic kinetic energy, represented by an equivalent temperature, as a function of time after femtosecond-laser excitation.

X and L points. Obviously, silicon does not predominantly melt in the direction of the lattice instability, which is surprising and in contrast to previous expectation [24,33].

Given our present result that the phonon frequencies in laser-excited silicon are mostly irrelevant for its ultrafast melting, we are led to the conclusion that the different melting ways reflect properties of the laser-excited potential energy surfaces beyond the harmonic approximation arising from both anharmonicities and couplings between phonon modes. The inset in Fig. 4(b) powerfully illustrates this for the X and L points: Whereas the interactions are attractive at the X and repulsive at the L point for small atomic displacements, this situation is reversed at larger displacements. We note that in Ref. [33] this has already been calculated for L without realizing its full relevance. We found that the barrier to escape the potential energy minimum in the X direction amounts to only 0.02 eV, which is smaller than the average initial thermal energy $k_B T_i = 0.027$ eV of each phonon. This explains why Si can melt predominantly at X in quasimomentum space. We predict, however, that an effect of the lattice instability becomes noticeable at low atomic temperatures, when the atoms are moving sufficiently close to their ideal positions. Indeed, additional *ab initio* molecular dynamics simulations, which we performed at 77 K and for $n = 9.7\%$, showed ultrafast melting mainly at L.

So far, we have analyzed the energy transfer to and between the atomic degrees of freedom during ultrafast melting in silicon by following the quasimomentum-resolved mean-square displacement of the atoms. In Fig. 5 we show the kinetic energy in the X and L points for the same excitation density as in Fig. 4 as a function of time after femtosecond-laser excitation. This energy is expressed as an equivalent temperature. We see that both points in quasimomentum space are initially in thermal equilibrium at room temperature. After excitation the X-point phonons rapidly reach a temperature of 1200 K. The L-point phonons also become hotter, but significantly less so. Figure 5 shows that the atomic displacements and kinetic energies are related and supports our above conclusion that energy does not predominantly flow in the direction of the lattice instability.

In conclusion, we analyzed the ultrafast energy exchange between atomic degrees of freedom by simulating ultrafast melting of silicon and surprisingly found that the melting ways can be very different, essentially depending on the excitation density. Our findings thus change the manner in which we understand laser-induced structural phenomena as exemplified by the solid-liquid transition in Si. We saw that the flow of energy to and between the atomic degrees of freedom, which are strongly coupled for the large atomic displacements that can be induced by an ultrashort laser pulse, were highly nontrivial, which has to be taken into account when modeling ultrafast phenomena. In particular, we found that the harmonic approximation breaks down for the description of the energy flow channels in laser excited Si. We further made the experience that the resolution of atomic displacements and energies according to quasimomentum is a very useful tool to obtain an informative and intuitively understandable image of the microscopic processes induced. We note that the resolution of the atomic pathways during ultrafast melting achieved in this work solves a long-standing open problem in the field of femtosecond-laser induced phenomena [24,33–36]. Our analysis of these paths in terms of the energy flow between atomic degrees of freedom can be directly measured by means of the novel technique of diffuse or background scattering [15–17].

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