Supplementary Materials for

The seeds and homogeneous nucleation of photoinduced nonthermal melting in semiconductors due to self-amplified local dynamic instability

Wen-Hao Liu et al.

Corresponding author: Jun-Wei Luo, jwluo@semi.ac.cn; Lin-Wang Wang, lwwang@semi.ac.cn

Sci. Adv. 8, eabn4430 (2022)
DOI: 10.1126/sciadv.abn4430

This PDF file includes:

Sections S1 to S4
Figs. S1 to S11
References
Section 1: rt-TDDFT methods for photoexcited dynamic simulations

In this rt-TDDFT algorithm, the time-dependent wave functions $\psi_j(t)$, are expanded by the adiabatic eigenstates, $\phi_i(t)$:

$$\psi_j(t) = \sum_i C_{ji}(t) \phi_i(t)$$  \hspace{1cm} (1)

and

$$H(t)\phi_i(t) = \epsilon_i(t)\phi_i(t)$$  \hspace{1cm} (2)

Here, $H(t) \equiv H(t, R(t), \rho(t))$, $R(t)$ represents the nuclear positions, and $\rho(t)$ represents the charge density. By using equation (1), the evolution of the wave functions $\psi_j(t)$ is changed to the evolution of the coefficient $C_{ji}(t)$. In equation (2), a linear-time-dependent Hamiltonian (LTDH) is applied to represent the time dependence of the Hamiltonian within a time step $[t_1, t_1 + \Delta t]$: For any $t \in [t_1, t_1 + \Delta t]$

$$H(t) = H(t_1) + \frac{t - t_1}{\Delta t} [H(t_1 + \Delta t) - H(t_1)]$$  \hspace{1cm} (3)

Thus, we can obtain a much larger time step (0.1 fs - 0.2 fs) than the conventional real-time TDDFT (sub-attosecond), and the time step is set to 0.1 fs in our simulation.

To mimic the photoexcitation, we add A-field in the $k$-space of Hamiltonian.

$$H(t) = 1/2(-i\nabla + A(t))^2$$  \hspace{1cm} (4)

For rt-TDDFT Hamiltonian, we further obtain,

$$H(t) = 1/2(-i\nabla_x + A_x \times E(t))^2 + 1/2(-i\nabla_y + A_y \times E(t))^2 + 1/2(-i\nabla_z + A_z \times E(t))^2$$  \hspace{1cm} (5)

In our work, we design $A_x = A_y = A_z$, so the electric field polarization is average along the $x, y,$ and $z$ directions. $E(t)$ is an external electric field of the time dimension to simulate a laser pulse with a Gaussian shape in our rt-TDDFT,

$$E(t) = E_0 \cos(\omega t) \exp[-(t - t_0)^2/(2\sigma^2)]$$  \hspace{1cm} (6)

$E_0$ is a constant in V/Å unit. We choose two group parameters in our simulations: $t_0 = 75$ fs, $\sqrt{2}\sigma = 25$ fs is the pulse width, and $\omega = 3.2$ eV is the photon energy which is consistent with a 387-nm
optical pump pulse in experiment (12); $t_0 = 50$ fs, $\sqrt{2}\sigma \approx 25$ fs is the pulse width, and $\omega = 2.03$ eV is the photon energy which is consistent with a 610-nm optical pump pulse in another experiment (13). Here, we adopt the different laser pulses to compare the two experimental data.

In our simulations, we corrected the DFT band gap to the experimental value for bulk Si by adding an additional exponential term $\alpha \times \exp(-(r/a)^2)$ ($a$ is Bohr radius) to the nonlocal potential projector $s(r)$ of the $3s$ orbital for Si atom. This method has been used in our previous paper (58). The modified potential in a small range near the nuclear is shown in Supplementary Fig. S1, and the modification most affects the unoccupied conduction band, thus having minimal effects on the phonon dynamics of the system (Supplementary Fig. S2). As one can see, the whole conduction band, including the direct band gap, and DOS have been pushed up, while the phonon spectrum is essentially unchanged. The DFT SCF calculation is based on this corrected pseudopotential. $\alpha=0$, corresponds to the original PBE potential, with DFT predicted band gap as 0.58 eV for bulk Si, and the band gap is 1.12 eV when $\alpha=0.9$. It was with this corrected pseudopotential we have carried out our TDDFT calculations.

Supplementary Figure 1 | Correlation of band gap for Si. The modified $s$ orbital potential of Si atom as a function of the radius $r$, which is in the unit of Bohr.
Supplementary Figure 2 | **Comparison of basic physical properties.** The band structure, density of state (DOS), and phonon dispersion curves in different band gap corrected by pseudopotential.

Supplementary Figure 3 | **Representations of structural change by pair distribution function (PDF).**

a, The case of 11% excitations. b, The case of 2300 K lattice temperature without any excitation.
Furthermore, we calculate the pair distribution function (PDF) of four snapshots, as shown in Supplementary Fig. S3. The PDF with a room temperature structure at an initial time has three sharp peaks around 2.35 Å, 3.85 Å, and 4.55 Å, which represents the distribution of neighbor, next-nearest neighbor, and third-nearest neighbor between Si atoms, respectively. To compare with the excitation-induced nonthermal melting result, we have also carried out a pure thermal melting (using ground state AIMD) result with an initial room temperature atomic position configuration, but a large nuclear kinetic energy (corresponds to a temperature of 2300 K). We see that, for the two cases, their initial ($t = 0$) PDFs are the same. But during the melting process (50 fs, 100 fs), the third peak is still clear for the nonthermal melting case, while it disappears quickly in the thermal melting case. This also means the nonthermal melting has a better long-range order, while with large disorder locally, in agreement with our local fluctuation picture. We hope the different PDFs can provide a way for future experimental verifications of our results.

**Supplementary Figure 4 | Simulation of a higher electronic excitation in Si.** (a) The density of state (DOS) of excited carriers as a function of time. Red (blue) shaded areas represent excited electron (hole) occupations. (b) Evolution of the number of excited electrons. The purple line shows a laser pulse. (c) Evolution of lattice temperature. (d) Evolution of band gap.
Supplementary Figure 5 | Si nonthermal melting in three exciting carrier distributions. **a**, Density of state (DOS) for distribution of excited carriers within three cases: valence electrons excited to conduction band edge with a longer laser wavelength (~610-nm) labeled by case 1 (green); photoexcitation by a 387-nm pump pulse labeled by case 1 (orange); the valence electrons excited to the higher energy levels labeled by case 3 (blue). Shaded areas represent excited electron and hole occupations. The VBM is set to 0 eV and CBM is 1.12 eV, respectively. **b**, The root-mean-square displacement (RMSD) as a function of time. The dashed line is the Lindemann criterion as a critical limit (approximately 15% of the Si-Si bond length 2.35 Å, i.e., \( R_c = 0.35 \) Å). **c**, RMSD as a function of time in 15%, 20%, and 25% excitations in Si. **d**, Si lattice temperature as a function of time, the dashed line is the Si melting point.

Supplementary Figure S5 shows three photoexcitation with the same number of electronic excitation but three different laser wavelengths, resulting in the almost same number of excited valence electrons but occupying different places in the conduction bands in three photoexcitation. We confirm that the nonthermal melting is indeed easy to occur when the excited electrons occupy the conduction band edge by the lower-frequency laser. The high-frequency laser prompts the same amount of valence electrons to occupy the higher-lying conduction band levels. Such photoexcitation increases the electron potential energy a lot but the nonthermal melting process takes a much longer time to begin and complete, which supports our conclusion. Note that, we do not consider other effects (like photoemission, and Auger decay) in the higher electronic distribution. However, if the photon fluence is large, we do see a faster melting in Supplementary Fig. 5c.
Section 2: Simulations of valence electrons constrained to the conduction band

Supplementary Figure 6 | Ultrafast dynamics with 11% of valence electrons fixed to the conduction band edge (CBE). a, Density of states (DOS) of Si. Shaded areas represent excited hole and electron occupations. The VBM is set to 0 eV and CBM is 1.12 eV, respectively. b, The snapshots of atomic displacements in the (x, y) plane at 0 fs, 20 fs, 40 fs, 50 fs, 60 fs, and 80 fs, respectively. The red atoms belong to the Lindemann particle \((R_i(t) - R_i(0) > 0.35 \text{ Å})\), which represents the molten atoms.

To further certify the homogenous nucleation mechanism, we design an initial electronic excitation state where the valence electrons near valence band edge (VBE) are moved to near conduction band edge (CBE), as shown in Supplementary Fig. 6a. Due to the PBE pseudopotential with 4 valence electrons in Si used in this study, the simulated 64-atoms system contains 256 valence electrons. Taking 11% excitations as an example, almost 28 electrons from the VBE are moved to the CBE. Based on the occupations of electronic excitations near CBE, we have re-run a simulation in a 300 K initial temperature. We find the Si crystal achieves the nonthermal melting within 80 fs. The nonthermal melting starts to occur in some local regions, then diffuses to the whole crystal, as shown in Supplementary Fig. 6b, which further proves the mechanism of local melting.
**Supplementary Figure 7 | Distribution of excited electrons (holes) and atomic driving force at an extremely low temperature (~ 1K).** a, c, e, g, for the case of valence electrons excited to lower levels; b, d, f, h, for the case of valence electrons excited to higher levels. a, b, Density of states (DOS) of Si. Shaded areas represent excited hole and electron occupations. c, d, Real-space distributions of excited electrons and holes at 0 fs and 200 fs. The accumulated electrons and holes at 200 fs are marked in red circles (Supplementary Fig. 6c), which induce the locally atomic distortion. e, f, Evolution of atomic driving force along x, y, z directions. The insets (Supplementary Fig. 6e) show the driving resultant force projected in the (x, y) plane at 0 fs and 200 fs, and the pink arrows represent the direction and magnitude of forces. g, h, Evolution of Si-Si bond length.

We constrain the valence electrons to near CBE and higher-energy levels as an initial state of electronic excitations, as shown in Supplementary Fig. 7a and 7b. To further verify the essence of nonthermal melting, we re-run the rt-TDDFT simulations at an extremely low temperature (~ 1K) to expulse the effect of thermally lattice vibrations. Initially, whether the excited electrons occupy the lower levels or the higher levels, the excited charge density is both high symmetry at $t = 0$ fs (Supplementary Fig. 7c and 7d), and the forces on atoms are zero (Inset in Supplementary Fig. 7e). In the case of excited electrons occupying CBE, the excited electrons and holes localize certain Si-Si bonds by charge transfer at 200 fs, marked in red circles (Supplementary Fig. 7c). The localized charge distributions trigger the microscopic driving forces along with the Si-Si bonding directions (Supplementary Fig. 7e), which induce the breaking of the Si-Si bond (Supplementary Fig. 7g). However, in the case of excited electrons occupying high-energy states, the excited carriers do not transfer certain Si-Si bonds. There are no corresponding atomic driving forces along Si-Si bonding directions (Supplementary Fig. 7f) to break the Si-Si bonds (Supplementary Fig. 7h).
Supplementary Figure 8 | Potential energy surfaces (PESs). The total energy of the Si system in different excitation states as a function of Si-Si bond length.

For the 610-nm case, they are excited to these states closer to the band edge, hence close to the bonding and antibonding states, while for the 387-nm case, the initial excited electrons and holes are in much higher energy states which cannot help with the Si-Si bond weakening. To further prove the conclusion, we apply the constrained DFT to calculate the potential energy surfaces (PESs) along Si-Si bond stretching at excitation-state occupations of 610-nm and 387-nm laser pumping, respectively (Supplementary Fig. 8). We find that occupying the electron states according to the 610-nm case can indeed reduce the local PES. But occupying the electron states according to the 387-nm case, the PES is hardly any effect. This means that ultrafast nonthermal melting is not manipulated by the increasing energy pumped into the system, rather the occupations of the special states (band-edge states) that are important for nonthermal melting.

According to the occupations of excited electrons from 610-nm and 387-nm laser pumping, we utilize constrained DFT to calculate the potential energy surfaces (PESs) along with Si-Si bond stretching (Supplementary Fig. 8). In the case of electrons occupying lower-energy levels (610-nm laser), the total energy gradually reduces along the Si-Si stretching direction which illustrates the initial ideal structure is unstable (Supplementary Fig. 8). In the case of electrons occupying higher energy levels, the total energy remains a minimum value at the ideal structure (Supplementary Fig. 8). By comparing the change PESs at different electronic occupations, we verify our conclusion again.
Section 3: Boltzmann-TDDFT methods

As discussed above, the original rt-TDDFT evolution does not satisfy the detailed balance, hence cannot be used to describe hot carrier cooling (60-62). The detailed balance is based on adiabatic states. Since we expand our wave function with the adiabatic states as shown in Eq.(2), this provides a unique opportunity for us in dealing with the detailed balance. To introduce detailed balance, we first need to define a charge flow between adiabatic states \(i\) and \(i'\). This can be defined as:

\[
T(i, i', t) = -\sum_{j=1}^{N} 2Re\{iC_{j,i}(t)V_{l,i'}(t)C_{j,i'}^{*}(t)\}
\]

(8)

Here \(V\) is the quantity in Eq.(3), and \(C_{j,i}\) is the wave function expansion coefficient. This \(T(i, i', t)\) describes the charge flow from adiabatic state \(i'\) to adiabatic state \(i\). This charge flow comes from all wave functions \(\psi_j(t)\), not just from any one of them. The \(T(i, i', t)\) is invariant under unitary rotations in the occupied subspace of \(\psi_j(t)\). Note: \(T(i, i', t) = -T(i', i, t)\). To introduce the decoherence effect, we first define time averaged \(T(i, i', t)\) as:

\[
I(i, i', t) = \frac{1}{\tau_{i,i'}} \int_{0}^{\infty} T(i, i', t - t') e^{-\frac{t'}{\tau_{i,i'}}} dt'
\]

(9)

Here \(\tau_{i,i'}\) is the decoherence time between adiabatic states \(i\) and \(i'\). Now, to restore the detailed balance, we like to change the time evolution Eq.(3), so the averaged charge flow from \(i'\) to \(i\) will be altered according to the detailed balance. To satisfy the detailed balance, we need to modify \(I(i, i', t)\) by adding a \(\Delta I(i, i', t)\) as:

\[
\Delta I(i, i', t) = \begin{cases} 
I(i, i', t)(e^{-|\epsilon_i - \epsilon_{i'}|/kT} - 1), & I(i, i', t)(\epsilon_i - \epsilon_{i'}) > 0 \\
0, & I(i, i', t)(\epsilon_i - \epsilon_{i'}) \leq 0 
\end{cases}
\]

(10)

Here \(\epsilon_i, \epsilon_{i'}\) are the adiabatic eigenstates, \(T\) is the temperature. Thus, \(\Delta I(i, i', t)\) can be considered as the correction to the charge flow \(T(i, i', t)\). This correction can be realized by modifying the wave function \(C_{j,i}(t)\) by adding a \(\Delta C_{j,i}(t)\) after every wave function evolution step from \(t_1\) to \(t_1+\Delta t\).

\[
\sum_{i=1}^{M} C_{j_1,i}(t) \Delta C_{j_2,i}^{*}(t) + \Delta C_{j_1,i}(t)C_{j_2,i}^{*}(t) = 0
\]

(11)
\[
2 \sum_{j=1}^{N} Re[C_{j,i}(t) \Delta C_{j,i}(t)] = \Delta t \sum_{i'} \Delta I(i, i', t)
\]  

(12)

The first equation is used to satisfy the orthonormal condition for \( \psi_j(t) \), while the second equation is used to modify the occupation of the adiabatic states by introducing \( \Delta I(i, i', t) \). The above linear equation is solved by the conjugate gradient method. Note that, usually there are more unknown parameters than the number of equations. Thus, minimum amplitude \( \Delta C_{j,i}(t) \) solution is sought which satisfies the above equations. After the introduction of \( \Delta C_{j,i}(t) \), the energy is not conserved. The energy conservation is restored by subtracting a velocity in the transition degree of freedom, which can be calculated from \( \Delta I(i, i', t) \) (46).

**Supplementary Figure 9 | Role of hot carrier cooling on Si structural nonthermal melting.** a, The simulated electron diffracted intensity of Si (220) Bragg peaks after 387-nm laser pulse pumping. The experimental data (gray circles) are from Si (220) peak with 11% electrons excited by 387-nm 150-fs pump
pulses. (13) b, Evolution of crystal temperature versus time. c, Evolution of band gap versus time. d, Real-space distributions of excited electrons (yellow color) and atomic structures (silver balls) at different times. e, for distributions of excited carriers as a function of time. Red (blue) shaded areas represent excited electron (hole) occupations.

Based on the new Boltzmann-TDDFT method, we have well described the effect of hot carrier cooling. In the NVE ensemble, the total energy is a constant, and the hot carriers transfer extra energy to cold lattice through electron-phonon (el-phon) coupling to increase the system temperature (Fig. 4). To separately illustrate the role of the carrier distributions in structural nonthermal melting, we can remove this hot carrier cooling to increase the lattice temperature by performing an NVT simulation, in which the system temperature is kept at 300 K (Supplementary Fig. 9b). As we can see in Supplementary Fig. 9a, the system is still broken around 500 fs (locally nonthermal distortion in Supplementary Fig. 9d) due to hot carrier cooling to band edge (Supplementary Fig. 9e). However, after that, as the electrons and holes fast recombine due to the disappearance of the bandgap (Supplementary Fig. 9c), the excited electrons go back to the ground state to reduce the driving force on Si atoms which results in the system returning to crystal structure at 1000 fs in Supplementary Fig. 9d.
Section 4. Simulations with a 216-atom supercell for Si.

Supplementary Figure S10 | Atomic dynamics of laser-induced ultrafast melting of Si with 216 atoms. 

a, Evolution of RMSD following the photoexcitation by a 610-nm 100-fs and a 387-nm 150-fs pump pulse. We carry out two rt-TDDFT simulations in a 387-nm 150-fs pump pulse: one takes into account the hot carrier cooling (red lines) and another has no carrier cooling, as in conventional rt-TDDFT simulations (blue lines). b, The rt-TDDFT simulation predicted electron diffracted intensity of Si (220) Bragg peaks. c,
Evolution of crystal temperature following the photoexcitation. **d-f**, Evolution of atomic structures in three rt-TDDFT simulations.

**Supplementary Figure S1**

Comparing the rt-TDDFT simulations from 64 atoms (black lines) and 216 atoms (red lines). **a,** The RMSD from a 2.03-eV photon energy laser pumping, and the evolution of lattice temperature is shown in **c.** **b,** The RMSD from a 3.2-eV photon energy laser pumping, and the evolution of lattice temperature is shown in **d.**

We have carried out additional rt-TDDFT simulations with a 216 Si atom supercell, as shown in supplementary Fig. 10. We also give a detailed comparison between 64-atom and 216-atom simulations in supplementary Fig. S11. It takes 15 days to simulate a timescale of 1.0 ps in our rt-TDDFT simulations by using 24 GPU for the 216 Si atom system. To the best of our knowledge, this is the largest system size for rt-TDDFT simulations. We can see from supplementary Fig. 10 and supplementary Fig. S11 that the new results with a 216-atom supercell all support our original conclusions. Quantitatively, the 64-atom and 216-atom simulations give roughly similar results (supplementary Fig. 11) although there are some fluctuations due to the statistical nature of the simulation. Thus, regarding the comparison with the experiments and to provide the qualitative pictures, our 64-atom simulation is converged.
REFERENCES AND NOTES

1. A. Rousse, C. Rischel, S. Fourmaux, I. Uschmann, S. Sebban, G. Grillon, P. Balcou, E. Förster, J. P. Geindre, P. Audebert, J. C. Gauthier, D. Hulin, Non-thermal melting in semiconductors measured at femtosecond resolution. *Nature* **410**, 65–68 (2001).

2. S. K. Sundaram, E. Mazur, Inducing and probing non-thermal transitions in semiconductors using femtosecond laser pulses. *Nat. Mater.* **1**, 217–224 (2002).

3. A. M. Lindenberg, J. Larsson, K. Sokolowski-Tinten, K. J. Gaffney, C. Blome, O. Synnergren, J. Sheppard, C. Caleman, A. G. MacPhee, D. Weinstein, D. P. Lowney, T. K. Allison, T. Matthews, R. W. Falcone, A. L. Cavalieri, D. M. Fritz, S. H. Lee, P. H. Bucksbaum, D. A. Reis, J. Rudati, P. H. Fuoss, C. C. Kao, D. P. Siddons, R. Pahl, J. Als-Nielsen, S. Duesterer, H. Schlarb, H. Schulte-Schrepping, T. Tschentscher, J. Schneider, D. von der Linde, O. Hignette, F. Sette, H. N. Chapman, R. W. Lee, T. N. Hansen, S. Techert, J. S. Wark, M. Bergh, G. Huldt, D. van der Spoel, N. Timneanu, J. Hajdu, R. A. Akre, E. Bong, P. Krejcik, J. Arthur, S. Brennan, K. Luening, J. B. Hastings, Atomic-scale visualization of inertial dynamics. *Science* **308**, 392–395 (2005).

4. M. Eichberger, H. Schäfer, M. Krumova, M. Beyer, J. Demsar, H. Berger, G. Moriena, G. Sciaini, R. J. D. Miller, Snapshots of cooperative atomic motions in the optical suppression of charge density waves. *Nature* **468**, 799–802 (2010).

5. G. Sciaini, R. J. D. Miller, Femtosecond electron diffraction: Heralding the era of atomically resolved dynamics. *Rep. Prog. Phys.* **74**, 096101 (2011).

6. T. Frigge, B. Hafke, T. Witte, B. Krenzer, C. Streubühr, A. Samad Syed, V. Mikšić Trontl, I. Avigo, P. Zhou, M. Ligges, D. von der Linde, U. Bovensiepen, M. Horn-von Hoegen, S. Wippermann, A. Lücke, S. Sanna, U. Gerstmann, W. G. Schmidt, Optically excited structural transition in atomic wires on surfaces at the quantum limit. *Nature* **544**, 207–211 (2017).
7. E. A. Seddon, J. A. Clarke, D. J. Dunning, C. Masciovecchio, C. J. Milne, F. Parmigiani, D. Rugg, J. C. H. Spence, N. R. Thompson, K. Ueda, S. M. Vinko, J. S. Wark, W. Wurth, Short-wavelength free-electron laser sources and science: A review. Rep. Prog. Phys. 80, 115901 (2017).

8. A. Kogar, A. Zong, P. E. Dolgirev, X. Shen, J. Straquadine, Y.-Q. Bie, X. Wang, T. Rohwer, I.-C. Tung, Y. Yang, R. Li, J. Yang, S. Weathersby, S. Park, M. E. Kozina, E. J. Sie, H. Wen, P. Jarillo-Herrero, I. R. Fisher, X. Wang, N. Gedik, Light-induced charge density wave in LaTe₃. Nat. Phys. 16, 159–163 (2020).

9. J. G. Horstmann, H. Böckmann, B. Wit, F. Kurtz, G. Storeck, C. Ropers, Coherent control of a surface structural phase transition. Nature 583, 232–236 (2020).

10. R. T. Young, C. W. White, G. J. Clark, J. Narayan, W. H. Christie, M. Murakami, P. W. King, S. D. Kramer, Laser annealing of boron-implanted silicon. Appl. Phys. Lett. 32, 139–141 (1978).

11. M. Combescot, J. Bok, Instability of the electron-hole plasma in silicon. Phys. Rev. Lett. 48, 1413–1416 (1982).

12. H. W. Tom, G. D. Aumiller, C. H. Brito-Cruz, Time-resolved study of laser-induced disorder of Si surfaces. Phys. Rev. Lett. 60, 1438–1441 (1988).

13. M. Harb, R. Ernstorfer, C. T. Hebeisen, G. Sciaini, W. Peng, T. Dartigalongue, M. A. Eriksson, M. G. Lagally, S. G. Kruglik, R. J. D. Miller, Electronically driven structure changes of Si captured by femtosecond electron diffraction. Phys. Rev. Lett. 100, 155504 (2008).

14. P. Stampfli, K. H. Bennemann, Dynamical theory of the laser-induced lattice instability of silicon. Phys. Rev. B Condens. Matter 46, 10686–10692 (1992).

15. P. Stampfli, K. H. Bennemann, Time dependence of the laser-induced femtosecond lattice instability of Si and GaAs: Role of longitudinal optical distortions. Phys. Rev. B Condens. Matter 49, 7299–7305 (1994).

16. P. L. Silvestrelli, A. Alavi, M. Parrinello, D. Frenkel, Ab initio molecular dynamics simulation of laser melting of silicon. Phys. Rev. Lett. 77, 3149–3152 (1996).
17. V. Recoules, J. Clerouin, G. Zerah, P. M. Anglade, S. Mazevet, Effect of intense laser irradiation on the lattice stability of semiconductors and metals. Phys. Rev. Lett. 96, 055503 (2006).

18. E. S. Zijlstra, A. Kalitsov, T. Zier, M. E. Garcia, Squeezed thermal phonons precurse nonthermal melting of silicon as a function of fluence. Phys. Rev. X 3, 011005 (2013).

19. N. Medvedev, Z. Li, B. Ziaja, Thermal and nonthermal melting of silicon under femtosecond x-ray irradiation. Phys. Rev. B 91, 054113 (2015).

20. C. Lian, S. B. Zhang, S. Meng, Ab initio evidence for nonthermal characteristics in ultrafast laser melting. Phys. Rev. B 94, 184310 (2016).

21. T. Pardini, J. Alameda, A. Aquila, S. Boutet, T. Decker, A. E. Gleason, S. Guillet, P. Hamilton, M. Hayes, R. Hill, J. Koglin, B. Kozioziemski, J. Robinson, K. Sokolowski-Tinten, R. Soufli, S. P. Hau-Riege, Delayed onset of nonthermal melting in single-crystal silicon pumped with hard x rays. Phys. Rev. Lett. 120, 265701 (2018).

22. R. Darkins, P.-W. Ma, S. T. Murphy, D. M. Duffy, Simulating electronically driven structural changes in silicon with two-temperature molecular dynamics. Phys. Rev. B 98, 024304 (2018).

23. N. Medvedev, M. Kopecky, J. Chalupsky, L. Juha, Femtosecond x-ray diffraction can discern nonthermal from thermal melting. Phys. Rev. B 99, 100303(R) (2019).

24. P. Saeta, J. Wang, Y. Siegal, N. Bloembergen, E. Mazur, Ultrafast electronic disordering during femtosecond laser melting of GaAs. Phys. Rev. Lett. 67, 1023–1026 (1991).

25. J. S. Graves, R. E. Allen, Response of GaAs to fast intense laser pulses. Phys. Rev. B 58, 13627–13633 (1998).

26. K. J. Gaffney, A. M. Lindenberg, J. Larsson, K. Sokolowski-Tinten, C. Blome, O. Synnergren, J. Sheppard, C. Caleman, A. G. MacPhee, D. Weinstein, D. P. Lowney, T. Allison, T. Matthews, R. W. Falcone, A. L. Cavalieri, D. M. Fritz, S. H. Lee, P. H. Bucksbaum, D. A. Reis, J. Rudati, A. T. Macrander, P. H. Fuoss, C. C. Kao, D. P. Siddons, R. Pahl, K. Moffat, J. Als-Nielsen, S. Dueinterer, R. Ischebeck, H. Schlarb, H. Schulte-Schrepping, J. Schneider, D. von der Linde, O. Hignette, F. Sette, H.
N. Chapman, R. W. Lee, T. N. Hansen, J. S. Wark, M. Bergh, G. Huldt, D. van der Spoel, N. Timneanu, J. Hajdu, R. A. Akre, E. Bong, P. Krejcik, J. Arthur, S. Brennan, K. Luening, J. B. Hastings, Observation of structural anisotropy and the onset of liquidlike motion during the nonthermal melting of InSb. *Phys. Rev. Lett.* **95**, 125701 (2005).

27. A. M. Lindenberg, S. Engemann, K. J. Gaffney, K. Sokolowski-Tinten, J. Larsson, P. B. Hillyard, D. A. Reis, D. M. Fritz, J. Arthur, R. A. Akre, M. J. George, A. Deb, P. H. Bucksbaum, J. Hajdu, D. A. Meyer, M. Nicoul, C. Blome, T. Tschentscher, A. L. Cavalieri, R. W. Falcone, S. H. Lee, R. Pahl, J. Rudati, P. H. Fuoss, A. J. Nelson, P. Krejcik, D. P. Siddons, P. Lorazo, J. B. Hastings, X-ray diffuse scattering measurements of nucleation dynamics at femtosecond resolution. *Phys. Rev. Lett.* **100**, 135502 (2008).

28. E. S. Zijlstra, J. Walkenhorst, M. E. Garcia, Anharmonic noninertial lattice dynamics during ultrafast nonthermal melting of InSb. *Phys. Rev. Lett.* **101**, 135701 (2008).

29. X. Wang, J. C. Ekström, Å. U. J. Bengtsson, A. Jarnac, A. Jurgilaitis, V. T. Pham, D. Kroon, H. Enquist, J. Larsson, Role of thermal equilibrium dynamics in atomic motion during nonthermal laser-induced melting. *Phys. Rev. Lett.* **124**, 105701 (2020).

30. C. W. Siders, A. Cavalleri, K. Sokolowski-Tinten, C. Tóth, T. Guo, M. Kammler, M. H. von Hoegen, K. R. Wilson, D. von der Linde, C. P. J. Barty, Detection of nonthermal melting by ultrafast X-ray diffraction. *Science* **286**, 1340–1342 (1999).

31. K. Sokolowski-Tinten, C. Blome, C. Dietrich, A. Tarasevitch, M. Horn von Hoegen, D. von der Linde, A. Cavalleri, J. Squier, M. Kammler, Femtosecond x-ray measurement of ultrafast melting and large acoustic transients. *Phys. Rev. Lett.* **87**, 225701 (2001).

32. J. A. Van Vechten, R. Tsu, F. W. Saris, D. Hoonhout, Reasons to believe pulsed laser annealing of Si does not involve simple thermal melting. *Phys. Lett. A* **74**, 417–421 (1979).

33. J. A. Van Vechten, R. Tsu, F. W. Saris, Nonthermal pulsed laser annealing of Si; plasma annealing. *Phys. Lett. A* **74**, 422–426 (1979).

34. C. V. Shank, R. Yen, C. Hirlimann, Time-resolved reflectivity measurements of femtosecond-optical-pulse-induced phase transitions in silicon. *Phys. Rev. Lett.* **50**, 454–457 (1983).
35. C. V. Shank, R. Yen, C. Hirlimann, Femtosecond-time-resolved surface structural dynamics of optically excited silicon. *Phys. Rev. Lett.* **51**, 900–902 (1983).

36. B. Rethfeld, K. Sokolowski-Tinten, D. von der Linde, S. I. Anisimov, Ultrafast thermal melting of laser-excited solids by homogeneous nucleation. *Phys. Rev. B* **65**, (2002).

37. M. Z. Mo, Z. Chen, R. K. Li, M. Dunning, B. B. L. Witte, J. K. Baldwin, L. B. Fletcher, J. B. Kim, A. Ng, R. Redmer, A. H. Reid, P. Shekhar, X. Z. Shen, M. Shen, K. Sokolowski-Tinten, Y. Y. Tsui, Y. Q. Wang, Q. Zheng, X. J. Wang, S. H. Glenzer, Heterogeneous to homogeneous melting transition visualized with ultrafast electron diffraction. *Science* **360**, 1451–1455 (2018).

38. S. R. Phillpot, S. Yip, D. Wolf, How do crystals melt? *Comput. Phys.* **3**, 20 (1989).

39. Z. Lin, L. V. Zhigilei, Time-resolved diffraction profiles and atomic dynamics in short-pulse laser-induced structural transformations: Molecular dynamics study. *Phys. Rev. B* **73**, (2006).

40. I. Inoue, Y. Deguchi, B. Ziaja, T. Osaka, M. M. Abdullah, Z. Jurek, N. Medvedev, V. Tkachenko, Y. Inubushi, H. Kasai, K. Tamasaku, T. Hara, E. Nishibori, M. Yabashi, Atomic-scale visualization of ultrafast bond breaking in x-ray-excited diamond. *Phys. Rev. Lett.* **126**, 117403 (2021).

41. P. Stampfli, K. H. Bennemann, Theory for the instability of the diamond structure of Si, Ge, and C induced by a dense electron-hole plasma. *Phys. Rev. B Condens. Matter* **42**, 7163–7173 (1990).

42. N. J. Hartley, J. Grenzer, L. Huang, Y. Inubushi, N. Kamimura, K. Katagiri, R. Kodama, A. Kon, W. Lu, M. Makita, T. Matsuoka, S. Nakajima, N. Ozaki, T. Pikuz, A. V. Rode, D. Sagae, A. K. Schuster, K. Tono, K. Voigt, J. Vorberger, T. Yabuuchi, E. E. McBride, D. Kraus, Using diffuse scattering to observe x-ray-driven nonthermal melting. *Phys. Rev. Lett.* **126**, 015703 (2021).

43. N. Medvedev, H. O. Jeschke, B. Ziaja, Nonthermal phase transitions in semiconductors induced by a femtosecond extreme ultraviolet laser pulse. *New J. Phys.* **15**, (2013).

44. T. Rohwer, S. Hellmann, M. Wiesenmayer, C. Sohrt, A. Stange, B. Slomski, A. Carr, Y. Liu, L. M. Avila, M. Kallâne, S. Mathias, L. Kipp, K. Rossnagel, M. Bauer, Collapse of long-range charge order tracked by time-resolved photoemission at high momenta. *Nature* **471**, 490–493 (2011).
45. C. W. Nicholson, A. Lücke, W. G. Schmidt, M. Puppin, L. Rettig, R. Ernstorfer, M. Wolf, Beyond the molecular movie: Dynamics of bands and bonds during a photoinduced phase transition. *Science* **362**, 821–825 (2018).

46. L. W. Wang, Natural orbital branching scheme for time-dependent density functional theory nonadiabatic simulations. *J. Phys. Chem. A* **124**, 9075–9087 (2020).

47. W.-H. Liu, Z. Wang, Z.-H. Chen, J.-W. Luo, S.-S. Li, L.-W. Wang, Algorithm advances and applications of time-dependent first-principles simulations for ultrafast dynamics. *WIREs Comput. Mol. Sci.* **12**, e1577 (2022).

48. K. Lu, Y. Li, Homogeneous nucleation catastrophe as a kinetic stability limit for superheated crystal. *Phys. Rev. Lett.* **80**, 4474–4477 (1998).

49. S. Mazevet, J. Clerouin, V. Recoules, P. M. Anglade, G. Zerah, Ab-initio simulations of the optical properties of warm dense gold. *Phys. Rev. Lett.* **95**, 085002 (2005).

50. Z. H. Jin, P. Gumbsch, K. Lu, E. Ma, Melting mechanisms at the limit of superheating. *Phys. Rev. Lett.* **87**, 055703 (2001).

51. W.-H. Liu, J.-W. Luo, S.-S. Li, L.-W. Wang, The critical role of hot carrier cooling in optically excited structural transitions. *npj Comput. Mater.* **7**, 117 (2021).

52. P. Yu, M. Cardona, *Fundamentals of Semiconductors* (Graduate Texts in Physics, Springer, 2010).

53. L. Waldecker, R. Bertoni, H. Hübener, T. Brumme, T. Vasileiadis, D. Zahn, A. Rubio, R. Ernstorfer, Momentum-resolved view of electron-phonon coupling in multilayer WSe2. *Phys. Rev. Lett.* **119**, 036803 (2017).

54. S. Wall, S. Yang, L. Vidas, M. Chollet, J. M. Glownia, M. Kozina, T. Katayama, T. Henighan, M. Jiang, T. A. Miller, D. A. Reis, L. A. Boatner, O. Delaire, M. Trigo, Ultrafast disordering of vanadium dimers in photoexcited VO2. *Science* **362**, 572–576 (2018).
55. Z. Wang, S. S. Li, L. W. Wang, Efficient real-time time-dependent density functional theory method and its application to a collision of an ion with a 2D material. *Phys. Rev. Lett.* **114**, 063004 (2015).

56. D. R. Hamann, Optimized norm-conserving Vanderbilt pseudopotentials. *Phys. Rev. B* **88**, 085117 (2013).

57. W. Jia, Z. Cao, L. Wang, J. Fu, X. Chi, W. Gao, L.-W. Wang, The analysis of a plane wave pseudopotential density functional theory code on a GPU machine. *Comput. Phys. Commun.* **184**, 9–18 (2013).

58. W.-H. Liu, J.-W. Luo, S.-S. Li, L.-W. Wang, Impurity diffusion induced dynamic electron donors in semiconductors. *Phys. Rev. B* **100**, 165203 (2019).

59. L. Zhang, W. Chu, C. Zhao, Q. Zheng, O. V. Prezhdo, J. Zhao, Dynamics of photoexcited small polarons in transition-metal oxides. *J. Phys. Chem. Lett.* **12**, 2191–2198 (2021).

60. J. Ren, N. Vukmirović, L.-W. Wang, Nonadiabatic molecular dynamics simulation for carrier transport in a pentathiophene butyric acid monolayer. *Phys. Rev. B* **87**, 205117 (2013).

61. P. V. Parandekar, J. C. Tully, Detailed balance in Ehrenfest mixed quantum-classical dynamics. *J. Chem. Theor. Comput.* **2**, 229–235 (2006).

62. P. V. Parandekar, J. C. Tully, Mixed quantum-classical equilibrium. *J. Chem. Phys.* **122**, 094102 (2005).