Molecular-dynamics thermal annealing model of laser ablation of silicon

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A molecular-dynamics thermal annealing model is proposed to investigate the mechanisms involved in picosecond pulsed laser ablation of crystalline silicon. In accordance with the thermal annealing model, a detailed description of the microscopic processes which result from the interaction of a 308 nm, 10 ps, Gaussian pulse with a Si(100) substrate has been embedded into a molecular-dynamics scheme. This was accomplished by explicitly accounting for carrier-phonon scattering and carrier diffusion. Below the predicted threshold fluence for ablation, \( F_{\text{th}} = 0.25 \text{ J/cm}^2 \), a surface breathing mode indicates that the solid restores internal equilibrium by the generation of pressure waves. Above \( F_{\text{th}} \), our simulations reveal that matter removal is triggered by subsurface superheating effects: intense heating of the material leads to the thermal confinement of the laser-deposited energy. As a result, the material is overheated up to a temperature corresponding to the critical point of silicon and a strong pressure gradient builds up within the absorbing volume. At the same time, diffusion of the carriers into the bulk leads to the development of a steep temperature gradient beneath the surface. Matter removal is subsequently driven by the relaxation of the pressure gradient: large pieces — several atomic layers thick — of molten material are expelled from the surface with initial axial velocities of \( \sim 1000 \text{ m/s} \), their ejection following the nucleation of voids beneath the surface.

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I. INTRODUCTION

The use of photons for the controlled removal of matter, i.e., laser ablation,1–3 has given rise to a large number of applications for materials processing and growth; in microelectronics, examples include surface micromachining, surface cleaning, and the pulsed laser deposition (PLD) of thin films, which allows a wide variety of materials to be grown.4 In spite of this, a complete picture of the mechanisms underlying ablation for a broad range of pulse durations and wavelengths, and for such diverse materials as metals, polymers and semiconductors, is still lacking.

The great complexity of phenomena involved in laser ablation, determined by the coupling of the laser pulse with the optical, elastic and thermal properties of the material, has been an obstacle in understanding. On a mesoscopic scale, the processes brought about by ultrashort — femtosecond — pulses have seldom been addressed.4 On the other hand, evidence of a competition between photomechanical and photothermal mechanisms has begun to emerge in the light-induced removal of matter with picosecond and nanosecond pulses. In the stress confinement regime, ejection of matter proceeds from photomechanical effects: energy is deposited in the material in a time shorter than that needed for the generation of acoustic waves, and ablation is induced by the relaxation of the pressure gradient that builds up within the absorbing volume. In the thermal confinement regime, energy is supplied to the irradiated volume at a rate faster than that at which it can be pumped out by thermal diffusion. Consequently, the material is rapidly brought near its critical point as matter removal is driven by photothermal effects: the metastable superheated liquid undergoes a prompt transition to a gaseous phase consisting, to a large extent, of molten micron-sized droplets. This mechanism is known as explosive boiling or phase explosion; other photothermal processes include vaporization and normal boiling (see Ref. 1 and references therein). Finally, there have been repeated reports8–10 of a fourth process known as subsurface superheating (SSSH). In this scenario, heating of the material causes vaporization as a result of which a steep temperature gradient develops beneath the surface. Matter removal then takes place in a manner similar to a phase explosion following the relaxation of the pressure build-up in the bulk. It is not clear whether this mechanism is real as conflicting views can be found in the literature.4

While it is generally assumed that the laser sputtering of metal surfaces involves phase explosion mechanisms (see, e.g., Ref. 17), both photomechanical and photothermal effects have been shown to be operative in organic solids.4 In semiconductor materials such as silicon, however, understanding of matter removal processes induced by picosecond pulses has yet to come. In the present study, we give evidence of a SSSH effect in the laser ab-
alation of silicon. This is achieved by carrying out detailed molecular-dynamics (MD) simulations of the interaction of a picosecond laser pulse with a Si(100) substrate, explicitly accounting for carrier-phonon scattering and carrier diffusion. It is assumed that the thermal annealing model (TAM) is valid so that thermal processes only are operative. In our computer code, ‘MADTAM’, we use the Stillinger-Weber (SW) potential to model the atomic interactions; preliminary results from an earlier version of our model can be found in Refs. 20 and 21.

Anticipating our results, we find that, below the (predicted) threshold fluence for ablation, \( F_{th} \), the solid restores internal equilibrium by the generation of pressure waves. Above \( F_{th} \), our simulations reveal that matter removal is triggered by SSH effects: intense heating of the material leads to the thermal confinement of the laser-deposited energy and a steep temperature gradient beneath the surface. Interestingly, the latter is not caused by the evaporation of atoms from the outer surface but, rather, originates from the process of carrier diffusion into the bulk. As a result, a strong pressure gradient builds up \( \sim 30 \) nm below the surface as the material is overheated up to a temperature corresponding to the critical point of silicon. Ablation is subsequently initiated by the relaxation of the pressure gradient: large pieces — several atomic layer thick — of molten material are expelled from the surface, a consequence of the nucleation of voids in the bulk. Before discussing these results, however, we give a detailed description of our model.

II. THE MODEL

The processing of silicon surfaces with femtosecond laser pulses involves ultrafast, non-thermal, phenomena which cannot be accounted for by the SW potential. For this reason, we remain within the picosecond regime where thermal mechanisms are involved; this is discussed in Sec. II A. A description of the computational method, i.e., molecular dynamics, follows in Sec. II B. Finally, the generation of electron-hole (e-h) pairs by photons, as well as their relaxation through carrier-phonon scattering and carrier diffusion, depicted in Fig. II, are detailed in Sec. II C to II E.

A. Preliminary considerations

Various computational techniques allow the interaction of light with matter to be simulated. Among them, MD appears to be a most suitable approach for addressing the numerous, complex processes involved in the laser ablation and desorption of matter: no hypotheses are needed to account for the various phenomena and atomic motion can be followed, in real time, provided that the interactions between the atoms are correctly modeled. However, because laser ablation involves large length and time scales, and thus a great computational effort, attempts involving classical MD are scarce. In order to extend the range of MD simulations, Zhigilei et al. proposed a breathing-sphere model appropriate to the study of matter removal in organic solids. In this work, the phase explosion due to overheating and the laser-induced pressure build-up were identified as the key processes responsible for ablation in the regimes of thermal and stress confinements, respectively.

Another MD study of laser ablation was performed by Herrmann et al., who examined the interaction of femtosecond laser pulses with silicon; a truncated version of the SW potential was used to account for the rupture of interatomic bonds following the absorption of photons. The predicted values of the threshold fluence for ablation thus obtained were at least an order of magnitude higher than those observed experimentally. This discrepancy is likely due to the inability of the SW potential to describe the non-thermal mechanisms involved in the interaction of femtosecond pulses with silicon. Indeed, it is generally agreed that there exists, for silicon, a critical carrier density \( n_c \sim 10^{22} \) cm\(^{-3}\) separating two distinct regimes:

(i) With picosecond and nanosecond pulses, carrier densities remain below the critical value and the relaxation is thermal, i.e., the carriers relax by transferring their kinetic energy to the lattice by the spontaneous emission of optical phonons in a characteristic time of \( \sim 1 \) ps. In this context, structural modifications such as melting and ablation are observed on a \( \sim 100 - 1000 \) ps time scale. This model, known as TAM, is suitable for laser pulses down to approximately 10 ps.

(ii) With femtosecond pulses, on the other hand, the number of free carriers may exceed \( n_c \) and ultrafast melting proceeds within \( \sim 1 \) ps by the collapse of the lattice. Because melting occurs before the carriers have time to relax through the emission of optical phonons, the relaxation is non-thermal. This model, first proposed by Van Vechten et al., is known as the plasma annealing model (PAM).

Furthermore, if the light intensity at the surface exceeds \( \sim 10^4 \) GW/cm\(^2\), the generation of a high number of energetic carriers through a two-photon absorption mechanism leads to the complete ionization of the material by avalanche ionization and/or field ionization: a very dense \( (n \geq 10^{23} \) cm\(^{-3}\)) and hot \( (\sim 10^6 \) K) e-h gas is generated near the surface. One then speaks of a solid-to-plasma transition as the material is carried away by the expanding plasma.

Here, because we make use of the SW potential, it is assumed that thermal processes only are operative; this restricts us to 10 ps or longer pulses. Care is taken to avoid carrier densities in excess of \( n_c \); in this context, the intensity remains well below \( \sim 10^4 \) GW/cm\(^2\).

B. Molecular dynamics
The MD technique has been discussed extensively in the literature (see, for instance, Ref. [32]). Briefly, the set of $3N$ Newton equations of motion, where $N$ is the number of atoms in the system, are solved from the knowledge of the interatomic forces. If $r_i$, $v_i$, and $a_i$ are the position, velocity and acceleration of the $i$th atom, respectively, the time evolution of the system is obtained by integrating, at discrete time steps, the following differential equations:

$$\frac{\partial r_i}{\partial t} = v_i,$$
$$\frac{\partial v_i}{\partial t} = a_i = -\frac{1}{m_i} \left[ \frac{\partial U(r_1, ..., r_N)}{\partial r_i} \right]_{r=r_i},$$  

given a set of initial positions and velocities $\{r_i^0, v_i^0\}$. In the above equations, $m_i$ is the mass of the $i$th atom and $U$ the interatomic potential. Thermodynamic quantities such as temperature and pressure can then be computed in a straightforward manner.[33]

All calculations were performed using the program groF, a general-purpose MD code for bulk and surfaces developed by one of the authors (LJL). The original form of the SW potential was used to compute the forces between the silicon atoms.[34] The equations of motion were solved using the velocity Verlet algorithm.[13] The MD time step was set to $\Delta t = 0.5$ fs for all simulations.

C. Target and laser pulse

Simulations are carried out for a supercell with approximate dimensions $3 \times 3 \times 60$ nm$^3$ (containing a total of 31680 atoms) representing a small volume of a Si(100) target located at the center of the laser pulse.

In order to recreate the thermal and structural constraints of a macroscopic crystal, the supercell is first repeated in the lateral ($x$ and $y$) directions using periodic boundary conditions (PBC). The thermal constraint is imposed by coupling a few monolayers of atoms at the bottom of the supercell to a heat reservoir; this is done by renormalizing the velocities to an appropriate Maxwell-Boltzmann (MB) distribution. These atoms also serve to minimize the reflection of pressure waves at the bottom of the supercell. This latter phenomenon affects the results by, in some cases, adding an artificial contribution to ablation. Though other techniques were proposed to attenuate such pressure waves,[35] the method described above gives satisfactory results. Additionally, a few monolayers of atoms attached to their equilibrium positions are placed beneath the heat reservoir in order to mimic a semi-infinite crystal. The crystal is assumed to be initially perfect.

The simulation of a 10 ps laser pulse, Gaussian in time as well as in the $x$ and $y$ directions and of macroscopic width, is accomplished assuming that any spatial variation of the irradiance can be neglected. This is valid because the laser spot diameter is assumed to be much larger than the region under study. The irradiance is thus, in effect, spatially constant over the infinite $x$-$y$ plane by virtue of the PBC.

The relatively large number of photons contained in a pulse, typically a few tens of thousands, ensures a uniform spatial distribution of the energy at the surface. The temporal Gaussian distribution is simulated by the successive arrival of planes of photons spanning the entire surface of the supercell, the number of which being determined by the instantaneous irradiance; they are separated in time by intervals ranging from $\Delta t$ to typically $10 \times \Delta t$.

D. Absorption of light

The absorption of light in silicon proceeds by the excitation of valence electrons via intraband and interband transitions, the frequency of which depends on several parameters, such as the density of free carriers and the wavelength and intensity of the laser pulse. The absorption of photons of energy $h\nu$ larger than the bandgap $E_g$ can induce three types of optical transitions: (i) An interband transition following the absorption of a single photon by a valence-band electron; a bond is broken and the electron is promoted to the conduction band, leaving a hole behind. The newly created pair shares an energy $\sim (h\nu - E_g)$, each carrier receiving an initial kinetic energy determined by the set of selection rules. (ii) A nonlinear, two- (or more) photon, interband transition, occurring when $n \geq 2$ photons are simultaneously absorbed. If $n \nu \geq \phi$, where $\phi = 4.85$ eV is the silicon work function,[40] the electron can be photoemitted; the condition $n \nu < \phi$, i.e., $\lambda > 255$ nm when $n = 1$, thus ensures that no photoemission takes place. (iii) An intraband transition, or free-carrier absorption, according to which the photon is absorbed by an electron already in the conduction band.

Following their creation, the carriers, because of momentum and energy conservation rules, occupy thin energy shells and a small volume of $k$ space. In a characteristic time $\tau_{ch}$ of typically a few tens of fs, the hole and electron subsystems achieve, through electron-hole scattering, a quasi-equilibrium state described by a Fermi-Dirac (FD) distribution at a common electronic temperature $T_e$, which is higher than the lattice temperature $T$. Thus, after $\sim 100$ fs, the carriers and the lattice constitute two decoupled subsystems, most of the energy remaining stored within the former ($T_e > T$).

If $n$ represents the conduction band carrier density, the balance equation for $e$-$h$ pairs can be written as

$$\frac{\partial n}{\partial t} + \nabla \cdot J = G + R ,$$  

where $J$ is the current density, $G$ the carrier generation rate resulting from the absorption of photons, and $R$ the net recombination rate given by

$$R = -\gamma n^3 + \delta(T_e)n ,$$  

where $\gamma$ is the capture rate resulting from Auger recombination, $\delta$ is a constant, and $T_e$ is the electron temperature. The factor $\gamma n^3$ accounts for the recombination rate resulting from the recombination of carriers with energy in excess of $E_g$, and $\delta(T_e)n$ is the thermal recombination rate. The balance equation for $e$-$h$ pairs can be written as

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with $\gamma$ the Auger recombination coefficient and $\delta(T_e)$ the impact ionization coefficient. The carrier generation rate $G$ is the sum of one- and two-photon processes, $G = G_1 + G_2$, and can be written as

$$G = \frac{(1 - \Gamma)\alpha I(z, t)}{h\nu} + \frac{(1 - \Gamma)^2 \beta I^2(z, t)}{2h\nu},$$  \hspace{1cm} (4)$$

$(1 - \Gamma)I(z, t)$ being the intensity of the laser at depth $z$ below the surface, $\Gamma$ the reflection coefficient at the surface, and $\alpha$ and $\beta$ the one-photon and two-photon interband absorption coefficients, respectively. The absorption proceeds according to the Beer-Lambert law

$$\frac{\partial I}{\partial z} = - (\alpha + \Theta n)I - \beta I^2,$$  \hspace{1cm} (5)$$

where $\Theta$ represents the free-carrier absorption cross-section.

It is instructive to compare the two-photon to one-photon carrier generation rates, that is the ratio

$$\frac{G_2}{G_1} = (1 - \Gamma)I(z, t)\left(\frac{\beta}{2\alpha}\right).$$  \hspace{1cm} (6)$$

If we choose $\lambda = 308$ nm, each photon carries an energy $h\nu = 4.03$ eV, larger than the bandgap of silicon at 300 K, $E_G \sim 1.12$ eV. For Si at 300 K, $\Gamma_0 = \Gamma T \sim (\Theta n) \alpha \sim 1.5 \times 10^6$ cm$^{-1}$ and $\beta \sim 40$ cm/GW. For an irradiance as high as $10^3$ GW/cm$^2$, a value at least an order of magnitude higher than the ones considered in this work, Eq. (6) gives $G_2/G_1 \lesssim 0.01$. Moreover, it has been shown that free-carrier absorption is negligible at short wavelengths, typically below 1000 nm. Therefore, the one-photon interband transition is the dominant mechanism for absorption in the present case and all other processes are ignored; as noted above, this allows the photoemission of electrons to be neglected.

In practice, upon arrival at the surface, the $x$-$y$ position of a photon is determined at random following a uniform probability distribution and reflected, again at random, according to

$$\Gamma(T) = \Gamma_0 + \Gamma_R \times T,$$  \hspace{1cm} (7)$$

where $\Gamma_R = 4 \times 10^{-5}$. Upon melting of the surface (see Sec. II A), the reflectivity is assumed to be that of l-Si, i.e., $\Gamma_L = 0.73$. If not reflected, the photon is absorbed in agreement with Eq. (4), neglecting two-photon and free-carrier absorption, at depth

$$z = -\alpha^{-1} \ln(\xi),$$  \hspace{1cm} (8)$$

where $\xi$ is a number generated from a uniform distribution; $\alpha$ is the absorption coefficient, given by

$$\alpha(T) = \alpha_0 \exp\left(\frac{T - \Theta_1}{\Theta_2}\right),$$  \hspace{1cm} (9)$$

where $\Theta_1 = 300$ K and $\Theta_2 = 4680$ K.

The silicon atom closest to the absorption site, and which possesses at least one valence electron, is then excited, i.e., its number of valence electrons is decremented by one. An $e$-$h$ pair is created with an initial position given by the $(x, y, z)$ coordinates of the excited atom. The relatively large absorption coefficient at $\lambda = 308$ nm, combined with a depth of 60 nm for the simulation box, ensures that more than 99% of the energy is absorbed within the supercell.

The determination of the exact initial kinetic energy of each carrier requires the knowledge of the allowed optical transitions. However, because very fast carrier-carrier scattering leads to a FD distribution at temperature $T_e$ within a few tens of fs, it is reasonable to assume the gas to be in a state of an instantaneous quasi-equilibrium. Further, because $T_e$ is relatively large, typically a few thousand degrees, the FD distribution is well approximated by a MB distribution. Thus, as an electron is promoted to the conduction band, its initial kinetic energy is calculated according to a MB distribution at the current temperature $T_e$. The problem of determining the set of optical transitions as well as the carrier density and temperature-dependent chemical potential, required to characterize a FD distribution, can thus be avoided. Using a Box-Muller transformation, a MB distribution at $T_e$ is obtained by calculating the electron initial kinetic energy, $E_{k_i}$, according to

$$E_{k_i} = -k_B T_e \sum_{i=1}^{3} \ln(\zeta_i) \cos^2(2\pi \xi_i),$$  \hspace{1cm} (10)$$

where $\zeta_i$ and $\xi_i$ are random numbers taken from a uniform distribution. The hole thus receives an initial kinetic energy equal to $(\nu - E_G - E_{k_i})$. The relationship used for $E_G$ (in eV) as a function of the lattice temperature $T$ and the carrier concentration $n$ is

$$E_G = E_G^0 - \frac{\kappa T^2}{(T + \Lambda)} - \zeta n^2,$$  \hspace{1cm} (11)$$

where $E_G^0 = 1.17$ eV, $\kappa = 4.730 \times 10^{-4}$ eV/K, $\Lambda = 636$ K and $\zeta = 1.5 \times 10^{-8}$ eV cm.

E. Relaxation processes

A number of microscopic mechanisms allow the system to restore equilibrium following irradiation by a laser pulse; these are carrier-phonon scattering, carrier diffusion, impact ionization and Auger recombination.

Impact ionization is the process through which an $e$-$h$ pair is created when an energetic electron collides with a valence electron: the former transfers part of its kinetic energy to the latter which is promoted to the conduction band. Because impact ionization most likely originates from the generation of highly-energetic carriers through two-photon interband transitions (negligible here; see Sec. III A) it can be ignored.
In Si, the dominant recombination mechanism is Auger \cite{59} for which the characteristic recombination time, due to screening effects at high carrier densities, is \( \geq 6 \) ps \cite{60}. Because the carrier density gradient, which develops at the surface following laser irradiation, is taken into account, in our model, by assuming a unidirectional flow of electrons and holes along the \( z \) axis into the bulk (see Sec. \( \text{II F} \)), the latter have usually diffused out of the simulation box in a time less than 6 ps. As a result, Auger recombination can also be neglected.

The important relaxation mechanisms, in the present context, are carrier-phonon scattering and carrier diffusion, which we explicitly take into account.

1. Carrier-phonon scattering

If the carrier density \( n \) remains below the critical value \( n_c \sim 10^{22} \text{ cm}^{-3} \), relaxation is thermal \cite{61}, i.e., the carriers relax by transferring their kinetic energy to the lattice by the spontaneous emission of (mainly) optical phonons in a characteristic time \( \tau_{LO} \sim 1 \) ps (also known as the carrier-phonon energy relaxation time \( \tau_E \)). The population of optical phonons thus increases for approximately 1 ps, after which the latter relax by emitting acoustic phonons in a characteristic time \( \tau_{PA} \sim 10 \) ps. Eventually, the energy is redistributed among all the vibrational modes of the lattice and a state of quasi-equilibrium is reached, characterized by a Bose-Einstein distribution at temperature \( T \). The further evolution of the system can then be described through thermal processes only as \( T \rightarrow T_c \), but \( T \) is still higher than its initial value.

There are several types of carrier-phonon scattering processes. It is possible to identify the most important ones, as well as their associated mean scattering rates. The dominant mechanisms for energetic electrons are the \( f \) and \( g \) intervalley scattering transitions, which involve large changes in momentum and thus acoustic or optical phonons with wave vectors near the zone boundary \cite{62}.

The probability \( P_{if} \) of observing a given intervalley transition, according to which a carrier in the valley \( i \), with crystal momentum \( \mathbf{p}_i \), scatters to a state with crystal momentum \( \mathbf{p}_f \) in the valley \( f \), is proportional to the square of the intervalley deformation potential \( D_{if} \), which characterizes the strength of the scattering \cite{63}. The probability can then be estimated as the weight associated with \( D_{if}^2 \). The probabilities thus obtained are listed in Table \( \text{I} \) and were calculated using the corresponding values for \( D_{if} \). As one can see, nearly 70% of phonons that scatter with electrons are optical. For holes, however, the main mechanism is optical deformation potential scattering \cite{64} and we thus assume the holes to scatter only with optical phonons of 62.6 meV \cite{65}. Moreover, the energy of the carrier determines whether scattering involves the absorption or the emission of a phonon. In Si, phonon emission is largely dominant for carrier energies exceeding \( E_s \sim 50 \) meV, while phonon absorption dominates below \( E_s \) \cite{66}.

To determine the rate at which the energy is transferred from the electronic to the ionic degrees of freedom, the mean carrier-phonon scattering rate as a function of carrier energy, \( 1/\tau_{cp}^0 \), is also needed. This quantity was calculated in Si at room temperature using the full bandstructure of the material by Fischetti \textit{et al.} \cite{67}. A fit to their data was embedded in our computer model; variations with temperature were ignored.

Because of screening effects, however, the observed carrier-phonon scattering rate decreases for carrier densities \( n \gtrsim 10^{21} \text{ cm}^{-3} \), as recently observed by Sjodin \textit{et al.} \cite{68}. Their results confirmed theoretical predictions by Yoffa \cite{69}. Screening effects were thus implemented in our model as suggested by Yoffa, with the new carrier-phonon scattering rate given by

\[
\tau_{cp}^{-1}(n) = \frac{\tau_{cp}^0}{\left( 1 + \left( \frac{n}{n_{sc}} \right)^2 \right)^2},
\]

where \( n_{sc} \sim 1.2 \times 10^{21} \text{ cm}^{-3} \) is the critical carrier density to observe significant screening effects; \( \tau_{cp}^0 \) is the value of \( \tau_{cp} \) without screening. Finally, the probability of an electron suffering a collision with a phonon was assumed to be Drude-like: the probability, \( P_s \), that a carrier has scattered with a phonon after a time \( t \), where \( t \) is the elapsed time since the last scattering event, is thus

\[
P_s(t) = 1 - \exp(-t/\tau_{cp}).
\]

In practice, we proceed as follows: after being generated, a carrier is given an initial position and kinetic energy as described in Sec. \( \text{II D} \), and its motion proceeds until a scattering event takes place. At each time step, the time elapsed since the last scattering event is determined, \( \tau_{cp} \) is computed and the probability \( P_s \) is determined from Eq. (13). If a scattering event occurs, a phonon is either emitted or absorbed depending if the carrier kinetic energy is greater or lower than \( E_s \), respectively.

For an \textit{electron} scattering with a phonon, the intervalley process is determined at random according to the probabilities of Table \( \text{I} \). A quantum of energy equal to \( h\omega_0 \) is then given to (phonon emission) or removed from (absorption) the lattice according to a spatial Gaussian distribution in a radius of 5 Å from the carrier, the latter value being an estimate of the carrier wave packet width based on the uncertainty principle. Though a finite duration is associated with each scattering event, the latter are assumed to be instantaneous for simplicity. Finally, if a phonon scattering event has occurred, the carrier energy is updated.

2. Carrier diffusion

Carriers diffuse into the bulk as a result of the density gradient, \( \nabla n \), which is itself a consequence of the exponentially-decreasing absorption with depth. The
variations with \( n \) of the ambipolar diffusion coefficient \( D \) and carrier mobilities, which characterize the dynamics of carriers in semiconductors, have been the subject of controversy: the available experimental data at densities exceeding \( 10^{19} \text{ cm}^{-3} \) are very scarce and concerns mostly germanium.

In fact, for \( n > 10^{19} \text{ cm}^{-3} \), it is not clear whether the ambipolar diffusion coefficient decreases due to additional carrier-carrier scattering, as proposed by Fletcher, or increases due to many-body quantum effects. At the same time, various models have been proposed using the expression suggested by Berz et al. to explain the influence of carrier-carrier scattering, as well as quantum effects, on \( D \).

Recent experimental data for moderate \( (10^{15} - 10^{17} \text{ cm}^{-3}) \) carrier densities tend to support Fletcher’s model. In view of this, and the lack of experimental evidence on many-body quantum effects for \( n > 10^{19} \text{ cm}^{-3} \), we adopt Fletcher’s model for \( D \) implemented in our code using the expression suggested by Berz et al.

Thus, each \( e\text{-}h \) pair is given an ambipolar diffusion coefficient which depends upon the local carrier density and local temperature, and which is updated at every time step, during which a carrier travels a distance \( \Delta z = \sqrt{D\Delta t} \) away from the surface.

### III. RESULTS AND DISCUSSION

All simulations were carried out assuming a laser pulse duration \( \tau_L = 10 \text{ ps} \) and photon energy \( h\nu = 4.03 \text{ eV} \) (\( \lambda = 308 \text{ nm} \)). The pulse intensity has a temporal Gaussian profile, but is spatially uniform. The fluence, \( F \), was varied between 0.01 and 0.75 J/cm\(^2\); corresponding intensities are in the range 1–75 GW/cm\(^2\).

In Sec. III A, we present our results for fluences of 0.01 to 0.20 J/cm\(^2\). No matter removal is observed; a breathing mode of the surface reveals the propagation of pressure waves in the solid. At and above \( F_{th} = 0.25 \text{ J/cm}^2 \), large pieces of molten material are expelled from the surface; the mechanisms by which they are ejected are examined in Sec. III B.

#### A. Below the threshold energy for ablation

Fig. 2 shows the carrier temperature \( T_c \) during the first two picoseconds for a fluence \( F = 0.05 \text{ J/cm}^2 \); \( T_c \) is obtained by summing the kinetic energies of the electrons and holes in the conduction and valence bands, respectively. The time evolution of the carrier density \( n \) and the surface, \( T_s \), and bulk, \( T_B \), values of the lattice temperature are shown in Fig. 3 for the same fluence; here, \( T_s \) is obtained by averaging over the first \( \delta = 1/\alpha \sim 7 \text{ nm} \) below the surface, where \( \delta \) is the optical skin depth, while \( T_B \) represents an average over the rest of the supercell. The pulse starts at \( t = 0 \) and the initial temperature of the target is \( \sim 300 \text{ K} \). Upon arrival of the first photons, \( T_c \) rises rapidly to \( \sim 11000 \text{ K} \) but \( n \) remains low: the pulse provides sufficient energy to create highly-energetic \( e\text{-}h \) pairs while not significantly increasing the number of carriers. The newly-generated hot electrons and holes promptly begin to thermalize with the lattice: within \( \sim 500 \text{ fs} \) to 1 ps, \( T_c \) drops to \( \sim 1500 \text{ K} \); this indicates a very fast initial cooling rate of the carriers through phonon scattering. For delays \( \gtrsim 1 \text{ ps} \), \( T_c \) decreases at a slower rate, i.e., the rate at which energy is being transferred from the electronic to the ionic degrees of freedom diminishes significantly. The carrier-phonon energy relaxation time, \( \tau_E \), is thus estimated to be a few hundreds fs. These observations are consistent with recent probing of ultrafast carrier dynamics in silicon by Goldman et al. who reported a value of \( \tau_E \sim 1 \text{ ps} \).

Equilibrium with the lattice is finally achieved after \( \sim 10 \text{ ps} \) with \( T_c \longrightarrow 300 \text{ K} \).

The carrier density \( n \) in Fig. 3 a reaches a peak at \( t \sim 7 \text{ ps} \), thus well after \( T_c \) has passed its maximum; this is because the \( e\text{-}h \) plasma loses energy to the lattice faster than it gains energy from the pulse. The decrease of \( n \) for \( t > 7 \text{ ps} \) is due to diffusion of the \( e\text{-}h \) pairs away from the surface; moreover, the carrier density remains well below the critical value, \( n_c \sim 10^{22} \text{ cm}^{-3} \), ensuring that the TAM is appropriate.

The pulse generates a high number of electrons and holes which, in turn, heat up the lattice; this is seen in Fig. 3 b. For \( t > \tau_L \), \( T_B \) reaches a plateau at \( \sim 1250 \text{ K} \); this value is below the melting temperature of c-Si, \( T_m = 1685 \text{ K} \). The surface temperature \( T_s \), on the other hand, continues to increase beyond \( \tau_L \), approaching \( T_B \) asymptotically. Most importantly, \( T_s < T_B \) for the whole duration of the simulation. This clearly indicates that the maximum lattice temperature is located beneath the surface, a direct consequence of carriers diffusing into the bulk as shown below.

The fact that the maximum temperature is found below the surface can be better appreciated from Fig. 4, where the lattice temperature \( T \) is plotted as a function of depth \( z \) at \( t = 50 \text{ ps} \) for a fluence \( F = 0.20 \text{ J/cm}^2 \); \( z = 0 \) corresponds to the surface. The temperature increases from a minimum of \( \sim 2000 \text{ K} \) at the surface to a maximum of \( \sim 4000 \text{ K} \) at \( z \sim 27 \text{ nm} \); the latter is above the boiling point \( T_b = 2753 \text{ K} \), but below the critical temperature, \( T_c = 5193 \text{ K} \), of silicon. For \( z \gtrsim 27 \text{ nm} \), \( T \) decreases. Thus, the maximum temperature is not occurring at the surface but, instead, at \( z \sim 30 \text{ nm} \). These observations can be explained as follows: the pulse intensity decreases exponentially with depth and, consequently, more \( e\text{-}h \) pairs are created near the surface (see Sec. III B). However, the time interval between two consecutive carrier-phonon scattering events being typically \( \sim 10 \text{ fs} \) to a few ps, a carrier will diffuse, on average, a few nm away from the surface between two scattering events. Thus, a large proportion of the energy is not released at the surface but, rather, deeper in the bulk.

Clearly, the temperature in Fig. 4 does not decay exponentially with depth, as one might have expected; rather, a steep temperature gradient has developed at \( z \lesssim 30 \text{ nm} \). This is a clear indication of SSSH effects.
which are usually assumed to originate from a vaporization process at the surface. However, it is important to note that, in our simulations, no vaporization is observed; this contrasts, for example, with the results of Zhigilei et al. who identified evaporation as the mechanism of matter removal below the threshold energy for ablation. The absence of evaporation in the present simulations is not surprising if one computes the flux (in atoms m\(^{-2}\) s\(^{-1}\)) of atoms that desorb from the surface, \(\Phi_e\), given by

\[
\Phi_e = \frac{P_e(T_e^z)}{\sqrt{2\pi M k_B T}} ,
\]

where \(M\) is the mass of a desorbed atom and \(P_e\) is the pressure of the vapor in equilibrium with the solid at a temperature \(T_e^z\). For \(F \gtrsim 0.12\) J/cm\(^2\), \(T_e \sim 2000\) K (see Fig. 3), \(P_e \sim 2.11\) Pa, and we find \(\Phi_e \sim 2.3 \times 10^{22}\) atoms m\(^{-2}\) s\(^{-1}\). The surface of the supercell has an area \(3 \times 3\) nm\(^2\) = \(9 \times 10^{-18}\) m\(^2\) and it is thus estimated that an atom desorbs every \(\sim 5\) \(\mu\)s, which is much longer than the duration of our simulations. Thus, the temperature profile in Fig. 4 cannot be explained by an evaporation process; rather, it is the result of carriers diffusing into the bulk.

Fig. 7 shows the surface temperature \(T_s\) as a function of fluence. The threshold for melting, \(F_m\), is thus estimated to be in the range 0.05–0.1 GW/cm\(^2\) since we must have \(T_s \geq T_m\) to observe melting. A more precise assessment of \(F_m\) is obtained by computing the coordination number averaged over the first few atomic layers below the surface, \(\rho_0\), as a function of time for various fluences. The results for \(F = 0.09\) J/cm\(^2\) are depicted in Fig. 8. A sudden change indicating the onset of melting is observed at \(t \sim 75\) ps: from \(\sim 3.88\) (a value slightly below that of bulk c-Si, a consequence of including in the calculation undercoordinated surface atoms), \(\rho_0\) approaches the coordination number of l-Si, i.e., \(\sim 6\). Because no significant changes in the surface coordination number are observed at lower fluences, the predicted threshold is thus \(F_m \sim 0.09\) J/cm\(^2\), melting taking place on a characteristic time of a hundred ps, in good agreement with experimental data.

The mechanisms by which the system restores internal equilibrium below \(F_{th}\) are revealed in Fig. 9 where the surface position, i.e., the \(z\) coordinate of the topmost atomic layer, \(z_{top}\), is plotted with respect to time for \(F = 0.10\) J/cm\(^2\); \(z_{top} = 0\) corresponds to the initial surface position. Also plotted is the bulk pressure \(P_B\), averaged over the entire supercell. As one can see, oscillations with an amplitude of \(\sim 1\) nm and a period \(\sim 30\) ps are observed at the surface. This breathing mode is due to the propagation of pressure waves in the solid; the latter represent the elastic response of the material to the intense heating by the pulse. Upon inspection of Fig. 9, \(P_B\) and \(z_{top}\) are clearly out of phase: because silicon expands when heated, \(z_{top}\) initially increases. At \(t \sim 20\) ps, \(z_{top}\) is maximum and \(P_B\) is minimum (\(P_B < 0\), tension); this is indicative of tensile stresses. In order to restore internal equilibrium, the material subsequently enters a compressive phase and contracts, i.e., \(z_{top}\) decreases. At \(t \sim 35\) ps, \(z_{top}\) is minimum and \(P_B\) is maximum (\(P_B > 0\), compression); the solid is then under compressive stresses. It is also apparent from Fig. 9 that melting occurs at the surface: the average value of \(z_{top}\) decreases with time, an indication that the material is more compact. Indeed, molten silicon is denser than crystalline silicon.

The surface velocity, \(v_{top}\), and acceleration, \(a_{top}\), computed from the data in Fig. 9, are found to be \(\sim 100\) m/s and \(\sim 10^{13}\) m/s\(^2\), respectively. These values are confirmed by noting that, upon heating, a surface undergoes an expansion \(\Delta z\) given by

\[
\Delta z = (1 - \Gamma)F_{\alpha T}/\rho C ,
\]

where \(\Gamma\) is the reflectivity, \(\alpha_T\) is the linear thermal expansion coefficient, \(\rho\) is the density and \(C\) is the specific heat. Assuming \(\Gamma \sim 0.59, \alpha_T \sim 2.6 \times 10^{-6}\) K\(^{-1}\), \(\rho \sim 2.33 g/cm^3, C \sim 0.713 J/gK^{-1}\), and a fluence \(F \sim 0.10\) J/cm\(^2\) at 300 K, Eq. (13) yields an oscillation amplitude \(\Delta z \sim 0.6\) nm, a value consistent with the results of Fig. 9. With a pulse duration \(t_L = 10\) ps, the velocity and acceleration of the surface become \(v_{top} \sim \Delta z/t_L \sim 60\) m/s and \(a_{top} \sim \Delta z/t_L^2 \sim 10^{13}\) m/s\(^2\), thus in good agreement with the above results. In addition, Fig. 8 gives the maximum value of \(v_{top}\) and \(a_{top}\) as a function of laser fluence. A maximum is observed at \(F = 0.15\) J/cm\(^2\). The subsequent decrease at \(F = 0.20\) J/cm\(^2\) might result from a stronger damping of the oscillations due to a thicker molten layer at the surface. Laser-induced oscillations at surfaces have found several applications. In dry laser cleaning, for instance, the removal of contaminants, i.e., adsorbed micron-sized particulates, is driven by momentum transfer: though of small amplitude (\(\sim 1\) nm), the surface oscillations take place on a very short time scale and thus exhibit very large accelerations.

Finally, Fig. 9 shows the pressure \(P\) as a function of depth \(z\) at \(t = 0\) and \(t = 10\) ps; the fluence is \(F = 0.10\) J/cm\(^2\). As expected, the pressure is zero throughout the material before laser irradiation. By the end of the laser pulse, a pressure gradient has built up at \(35 \lesssim z \lesssim 40\) nm; we show in Sec. 11B that the latter is responsible for matter ejection at fluences \(F \gtrsim 0.25\) J/cm\(^2\). Below the threshold energy for ablation, however, the pressure gradient is not high enough to cause ejection of matter, and the system relaxes through the generation of pressure waves.

### B. Above the threshold energy for ablation

The threshold energy for ablation, \(F_{th}\), is defined in this work as the minimum fluence for the onset of matter removal. No evaporation is observed (see Sec. 11A); rather, a collective ejection process is obtained at all flu-
ences above \( F_{th} \). Here, \( F_{th} = 0.25 \, \text{J/cm}^2 \), corresponding to a laser intensity \( I_{th} = 25 \, \text{GW/cm}^2 \).

Fig. 10 shows the surface position, \( z_{top} \), as a function of time for a fluence \( F = 0.35 \, \text{J/cm}^2 \). As is the case for \( F < F_{th} \), the material initially expands upon heating. However this does not result, this time, in a surface breathing mode. Instead, a dramatic change occurs at \( t \approx 30 \, \text{ps} \): from a value of \( \sim 7 \, \text{nm} \), \( z_{top} \) drops to \( \sim -35 \, \text{nm} \) within a few ps. This indicates that ablation has taken place over a depth \( h \sim 35 \, \text{nm} \), a value consistent with experiment. No significant change of \( h \) is observed at higher fluences.

A snapshot of the ablation process at \( t = 33 \, \text{ps} \) for the same fluence is given in Fig. 11. The photons were incident from the top. The atoms that have absorbed at least one photon are colored in dark gray, others are in light gray. Evidently, most photons have been absorbed near the surface.

Two features should be noted: (i) Ablation is a bulk phenomenon, i.e., the ejection of matter originates in the bulk and not at the surface as one might have expected. More specifically, ablation results in the expulsion of a large piece — a few tens of nm thick — of molten material from the surface with an initial axial velocity of \( \sim 1000 \, \text{m/s} \). (ii) As opposed to a disordered network in the bulk, a few nm thick crystalline layer is visible at the surface. The thickness of the latter corresponds to the average distance, about 5 nm, carriers created at the surface travel before suffering a first collision. For \( z \gtrsim 5 \, \text{nm} \), the temperature rises rapidly and, as shown below, the thickness of the layer removed during ablation depends upon the location of the pressure build-up in the bulk.

Insight into the mechanisms responsible for ablation is found in Fig. 12 showing the pressure, \( P \), and the lattice temperature, \( T \), as a function of depth for \( F = 0.35 \, \text{J/cm}^2 \). A steep temperature gradient has developed at the surface when \( t = 10 \, \text{ps} \), Fig. 12a; from a value of \( \sim 2000 \, \text{K} \) at \( z = 0 \), \( T \) rises rapidly to reach a plateau slightly above the critical temperature, \( T_c \), for \( z \sim 30 \, \text{nm} \). As shown in Sec. IIIA, the occurrence of a maximum temperature below the surface is not a consequence of evaporation from the surface, nor does it result from a thermal diffusion process carried by phonons. Rather, the energy is transported into the bulk by the electronic degrees of freedom; this mechanism is, of course, absent in organic solids.

Intense heating by the pulse leads to the thermal confinement of the laser-deposited energy and, as shown in Fig. 12h, the material is heated far beyond its boiling point by the end of the pulse. At the same time, the lattice cannot undergo sufficient thermal expansion and a strong pressure (\( > 0 \)) in excess of 10 GPa develops at \( 35 \lesssim z \lesssim 50 \, \text{nm} \), Fig. 12b. By \( t \approx 24 \, \text{ps} \) the latter has relaxed, leaving important tensile stresses in the material; these are responsible for the rapid expansion observed for \( t \gtrsim 10 \, \text{ps} \) in Fig. 10. The pressure profile at \( t = 24 \, \text{ps} \) in Fig. 12c also reveals a local minimum (in absolute value) at \( z \sim 35 \, \text{nm} \). As a consequence, strong tensile forces of opposite directions drive the material apart locally and nucleation of voids occur, as depicted in Fig. 13. The latter begins to form at \( t = 27 \, \text{ps} \) and ablation follows a few ps later as the mechanical strength of the material is exceeded.

As seen above, the high compressive stress which develops within the absorbing volume is responsible for the subsequent tensile forces; thus, it is the driving force responsible for matter removal above \( F_{th} \). Fig. 14 shows the variation of the maximum compressive stress, \( \sigma_{max} \), with laser fluence. Below the threshold for ablation, \( \sigma_{max} \) increases with \( F \). Above \( F_{th} \), however, \( \sigma_{max} \) saturates.

In a recent study of organic solids, Zhigilei et al. reported the observation of void nucleation in the stress confinement regime and attributed it to the build-up of a strong pressure gradient within the absorbing volume. The condition of stress confinement is expressed by \( \tau_L < \tau_S \sim \delta/\nu_S \), where \( \nu_S \) is the velocity of sound in the material. For c-Si, \( \nu_S \sim 9 \times 10^5 \, \text{m/s} \) and for a laser pulse at \( \lambda = 308 \, \text{nm} \), \( \tau_S \sim 1 \, \text{ps} \). This value is \( < \tau_L \) by a factor of 10; conditions of stress confinement are thus unlikely to develop in silicon following irradiation with 10 ps or longer pulses. The regime of thermal confinement, on the other hand, is expressed by \( \tau_L < \tau_S \sim \delta^2/D_T \), where \( D_T \) is the thermal diffusivity.

For silicon at 300 K, \( D_T \sim 0.86 \, \text{cm}^2/\text{s} \); this corresponds to \( \tau_S \sim 0.5 \, \text{ps} \), a value which is also an order of magnitude lower than \( \tau_L \). However, \( D_T \) drops to \( \sim 0.1 \, \text{cm}^2/\text{s} \) as \( T \) reaches \( 

IV. CONCLUDING REMARKS

A molecular-dynamics thermal annealing model (MADTAM) has been applied to the study of laser ablation of silicon with picosecond pulses on a 100 ps time scale. A detailed description of the thermal annealing model on a microscopic scale has been embedded into a molecular-dynamics scheme; this was accomplished by explicitly accounting for carrier-phonon scattering and carrier diffusion.
The model predicts a melting threshold \( F_m = 0.09 \, \text{J/cm}^2 \) and an ablation threshold \( F_{th} = 0.25 \, \text{J/cm}^2 \). Below \( F_{th} \), oscillations of the surface reveal the propagation of pressure waves in the solid. Above \( F_{th} \), important subsurface superheating (SSSH) effects are responsible for matter removal: as a result of the thermal confinement of the laser-deposited energy, the material is overheated to a temperature corresponding to the critical point of silicon and a pressure gradient builds up a few tens of \( \mu \text{m} \) beneath the surface. Ejection of matter is initiated by the relaxation of the strong compressive stresses after a few tens of ps, large pieces of molten material being expelled from the surface with high axial velocities.

We are currently investigating the role of surface effects. These are believed to be responsible for the formation of a surface space charge layer which is expected to influence the carrier dynamics and to compete with carrier diffusion.

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TABLE I: Probabilities $P_{ij}$ associated with the intervalley processes.

| $\omega_0$ (meV) | $D_{ij}$ ($10^8$ eV/cm) | $P_{ij}$ |
|------------------|-------------------------|---------|
| $f_3$ 62.6 (LO,TO)$^a$ | 1.75$^b$ | 0.344 |
| $g_1$ 44.3 (TA)$^b$ | 1.18$^b$ | 0.156 |
| $g_2$ 22.1 (LA)$^b$ | 1.18$^b$ | 0.156 |
| $g_3$ 62.6 (LO)$^a$ | 1.75$^b$ | 0.344 |
| Total | | 1.000 |

$^a$Ref. 47.
$^b$Ref. 56.

FIG. 1: Generation of an $e$-$h$ pair and the main subsequent relaxation mechanisms in MADTAM. (a) creation of an $e$-$h$ pair upon absorption of a photon; (b) scattering of the electron or hole by a phonon; (c) unidirectional diffusion of the $e$-$h$ pair into the bulk along the $z$ axis.
FIG. 2: Carrier temperature $T_e$ as a function of time for a fluence $F = 0.05 \text{ J/cm}^2$.

FIG. 3: (a) Carrier density $n$ and (b) surface $T_s$ and bulk $T_B$ temperatures as a function of time for a fluence $F = 0.05 \text{ J/cm}^2$. 
FIG. 4: Lattice temperature $T$ as a function of depth at $t = 50$ ps. The fluence is $F = 0.20 \text{ J/cm}^2$.

FIG. 5: Surface temperature $T_s$ as a function of laser fluence.

FIG. 6: Average surface coordination number $\rho_0$ as a function of time for a fluence $F = 0.09 \text{ J/cm}^2$. 
FIG. 7: Surface position $z_{\text{top}}$ and bulk pressure $P_B$ as a function of time for a fluence $F = 0.10 \text{ J/cm}^2$.

FIG. 8: Maximum velocity and maximum acceleration of the surface for different fluences.
FIG. 9: Pressure $P$ as a function of depth at different times. The fluence is $F = 0.10 \text{ J/cm}^2$.

FIG. 10: Surface position $z_{\text{top}}$ as a function of time. The fluence is $F = 0.35 \text{ J/cm}^2$. 
FIG. 11: Snapshot of the target at $t = 33$ ps illustrating matter removal. Atoms that have absorbed a photon are depicted in dark gray; others are in light gray. The lateral and vertical dimensions are $\sim 3$ nm and $\sim 40$ nm, respectively. The fluence is $F = 0.35$ J/cm$^2$. 
FIG. 12: (a) Lattice temperature $T$ as a function of depth at $t = 10$ ps and (b) pressure $P$ at different times as a function of depth. The fluence is $F = 0.35$ J/cm$^2$. 
FIG. 13: Snapshots of the subsurface region at a depth $30 \lesssim z \lesssim 40$ nm. The surface (not shown here) is above. Atoms that have absorbed a photon are depicted in dark gray; others are in light gray. The strong tensile stresses are responsible for void nucleation beneath the surface. The fluence is $F = 0.35 \text{ J/cm}^2$.

FIG. 14: Maximum compressive stress $\sigma_{max}$ below the surface as a function of fluence.