Short-Pulse Laser Ablation of Solids: From Phase Explosion to Fragmentation

Patrick Lorazo,[1,2,*] Laurent J. Lewis,[2] and Michel Meunier[1]

[1]*Département de Génie Physique et Groupe de Recherche en Physique et Technologie des Couches Minces (GCM), École Polytechnique de Montréal, C.P. 6079, Succursale Centre-Ville, Montréal, Québec, Canada, H3C 3A7*

[2]*Département de Physique et Groupe de Recherche en Physique et Technologie des Couches Minces (GCM), Université de Montréal, C.P. 6128, Succursale Centre-Ville, Montréal, Québec, Canada H3C 3J7*

(Received 23 October 2002; revised manuscript received 29 July 2003; published 25 November 2003)

The mechanisms of laser ablation in silicon are investigated close to the threshold energy for pulse durations of 500 fs and 50 ps. This is achieved using a unique model coupling carrier and atom dynamics within a unified Monte Carlo and molecular-dynamics scheme. Under femtosecond laser irradiation, isochoric heating and rapid adiabatic expansion of the material provide a natural pathway to phase explosion. This is not observed under slower, nonadiabatic cooling with picosecond pulses where fragmentation of the hot metallic fluid is the only relevant ablation mechanism.

DOI: 10.1103/PhysRevLett.91.225502 PACS numbers: 61.80.Az, 79.20.Ds, 79.20.Ap

Laser ablation is the process by which macroscopic amounts of material are ejected from the surface of a solid irradiated by a short, intense, laser pulse. In spite of its ubiquitous nature in many areas of technology [1], a satisfactory understanding of the fundamentals of laser ablation has been hampered by a complex phenomenology involving multiple length and time scales [2].

In metals and semiconductors, below the threshold energy for dielectric breakdown and plasma formation ($I_p \sim 10^{13}$ W/cm^2) [2,3], it is often argued that a system is pushed into the metastable region as a result of *rapid heating* [4–7]; phase separation follows from large, local, density fluctuations, i.e., homogeneous bubble nucleation in the metastable (superheated) liquid. This process, known as phase explosion or explosive boiling, has often been suggested based on the observation of liquid droplets in the plume for typical pulse durations of $\sim$10 ns [8]. However, the above interpretation fails for ultrashort ($\lesssim$1ps) pulses where heating is isochoric and explosive boiling takes place, instead, as the system adiabatically *cools* into the metastable region [2,9]. Moreover, using molecular dynamics (MD) and a simple Lennard-Jones model, Perez and Lewis have established the occurrence of fragmentation in the fs regime, thereby revealing a new path for the ejection of liquid droplets [9,10]. Thus, if a clear picture of ultrashort-pulse laser ablation is beginning to emerge, a definite assessment for longer (ps to ns) pulses has yet to come.

In this Letter, we report on the fundamental mechanisms of matter removal during short-pulse laser irradiation of Si for energies close to the ablation threshold but below that for plasma formation. Using a combined MD and Monte Carlo (MC) approach capable of capturing both microscopic and mesoscopic-scale dynamics, we follow the thermodynamic trajectory of the system in the temperature-density (ρ-T) plane during heating, expansion, and cooling for pulse durations of 500 fs and 50 ps. We show that, in spite of similarities between the expanding plumes (see Fig. 1), the mechanisms of matter removal are fundamentally different. In brief, rapid heating is observed to pull the system *away* from the metastable region, in contrast to the scenario reported in, e.g., Ref. [4]. The extent to which thermal diffusion takes place as the system subsequently cools towards the liquid-gas regime is found to be determinant for the ablation process. As shown below, this suggests a pulse duration upper limit for phase explosion of $\sim 10^{-11}$ s.

A complete description of our model will be given elsewhere. In short, classical MD is used to follow the motion of atoms which interact via the Stillinger-Weber (SW) potential [11]. Two systems, consisting of 99 000

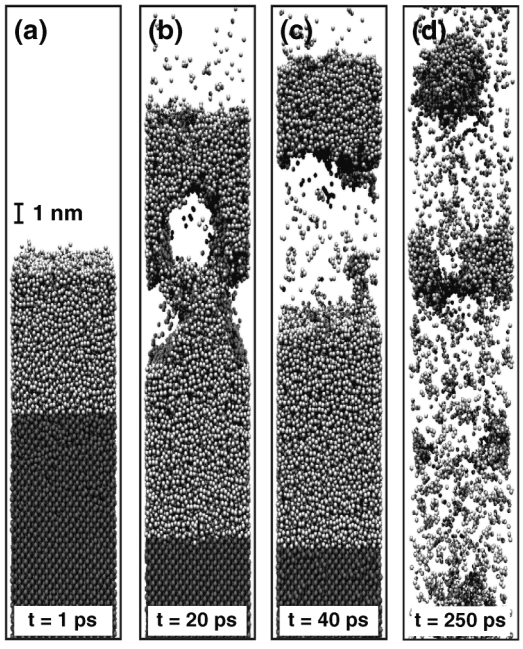

FIG. 1. Snapshots showing the ejection of molten material for two pulse durations at 266 nm: (a)–(c) 500 fs at a fluence of 0.375 J/cm^2; (d) 50 ps at a fluence of 0.55 J/cm^2; each pulse begins at $t = 0$. Dark gray: crystalline silicon; light gray: (metallic) liquid silicon.

($8 \times 8 \times 30\ \mathrm{nm}^3$) and 165 600 ($8 \times 8 \times 50\ \mathrm{nm}^3$) atoms embedded into a $8 \times 8 \times 500\ \mathrm{nm}^3$ supercell, are used for pulse durations of 500 fs and 50 ps, respectively. Periodic boundary conditions are applied in the x and y directions. In the z direction, normal to the surface, we proceed as follows: (i) to simulate heat diffusion into an infinite bulk, the crystal is terminated by a Langevin heat bath [12]; (ii) to mimic the propagation of pressure waves beyond the bottom of the supercell, a single atomic layer, to which an appropriate set of forces are applied, is added [6].

The laser pulse of duration τ_L (FWHM) has $\lambda_L = 266$ nm ($h\nu = 4.66$ eV) and is Gaussian in time but spatially constant; it is simulated by the successive arrival of photons which couple to "carriers." Here, a carrier is a particle (electron or hole) which follows Drude dynamics while undergoing various scattering events, each with its own characteristic collision time τ. The position at which a photon is absorbed along the z axis is determined from Beer's law, i.e., it has a probability $1 - \exp(-\alpha l_c)$ of being absorbed within each of the cells of side $l_c \sim 5$ Å dividing the supercell; α is the local absorption coefficient with contributions from interband and intraband transitions [$\sim(5\mathrm{nm})^{-1}$ for c-Si and l-Si]. In an interband event, an electron-hole pair is created with total kinetic energy $h\nu - E_G$, where E_G is the band gap energy: each carrier is given velocity $\mathbf{v}$ and kinetic energy $m^*v^2/2$, where the effective mass m^* (the only free parameter in the model) is chosen such as to reproduce the experimental melting threshold fluence at λ_L and $\tau_L = 15$ ps [13]. In an intraband transition, which is the only absorption process in the metallic molten material (see below), the carrier energy is increased by $h\nu$.

As mentioned above, the hot electrons and holes relax through a cascade of scattering events [1]. This is taken into account using a standard MC approach [14]. In the present model, carrier-carrier scattering allows carriers to exchange energy ($\tau_{\mathrm{c\text{-}c}} \sim 10$ fs, [1]). Heating, and eventually equilibrium at a common lattice (T) and electronic (T_e) temperature, is achieved through carrier-phonon scattering whereby a quantum of energy of 62.6 meV (c-Si, [14]) or 50 meV (l-Si) is given to nearby atoms if $T_e > T$ ($\tau_{\mathrm{c\text{-}ph}} \sim 10$ fs, [15]). In the crystal, additional scattering processes include Auger recombination and impact ionization [16]. As a final point, Si, like other group IV and III-V semiconductors, is metallic in the liquid state [17]: coordination increases from 4 to 6 and the electron density jumps to $\sim 10^{23}\ \mathrm{cm}^{-3}$. In our model, the semiconductor-to-metal transition is simulated by generating electrons (up to four per atom) at the rate at which the local coordination increases.

All simulations started from a Si(100) substrate at 300 K. Figures 1(a)–1(c) display the early stages of matter removal for a 500 fs pulse slightly above the threshold fluence for ablation, $F_{\mathrm{th}}^a = 0.35\ \mathrm{J/cm}^2$; the corresponding irradiance is $7 \times 10^{11}\ \mathrm{W/cm}^2$, well below I_p. About 1 ps after the beginning of the pulse, a hot ($\sim$8000 K) and highly pressurized ($\sim$10 GPa) liquid layer has formed at the surface [Fig. 1(a)]. The subsequent scenario is as follows: (i) more solid material is transformed into a liquid metal as the melt front propagates further into the bulk; (ii) closer to the surface, the relaxation of the pressure buildup within the liquid layer causes the latter to rapidly expand into vacuum, eventually leading to void nucleation [Fig. 1(b)] and to the ejection of a large piece of material with a velocity ≈ 200 m/s [Fig. 1(c)], i.e., ablation occurs. Note that the strongly excited Si crystal may, under fs laser irradiation, undergo an ultrafast, nonthermal melting transition which cannot be accounted for by empirical potentials such as SW [2]. Although the details of the energy deposition may depend on the path from solid to liquid, this is not expected to influence the *nature* of the ablation process occurring on much longer time scales.

As proposed in Ref. [9], it is possible to *directly* determine the mechanisms of matter removal by following the time evolution of the system in the ρ-T plane. To this effect, three distinct thermodynamic trajectories are computed: macroscopic (or average), dense (solid and/or liquid), and gas. This approach differs from other MD studies where the ablation mechanisms have been qualitatively assessed from a visual inspection of the plume [6].

A typical trajectory for the 500 fs pulse is given in Fig. 2(a). The starting point is a crystal at $\rho_0 = 2.33\ \mathrm{g/cm}^3$ and $T = 300$ K (marked A). The incoming laser energy is transferred to the ions in about 1 ps. No significant expansion occurs on this time scale and the result is a hot metallic liquid at high pressure and $\rho \approx \rho_0$ (B). The pressure is then released via mechanical expansion and the liquid-gas regime is approached as the system adiabatically *cools*. The rapidly expanding material, eventually entering the metastable region (C), is pushed close to the spinodal limit (dashed line) and homogeneous nucleation of gas bubbles in the superheated liquid takes place. This is indicated by the separation of the dense and macroscopic branches (D) and the concomitant appearance of a gas branch, thus revealing a decomposition of the metastable phase into a mixture of liquid and gas (D $\rightarrow$ E). Two remarks are in order: (i) the same trajectory can also be plotted in the T-P plane (see inset); this allows a direct comparison with the thermodynamic pathway proposed by Miotello and Kelly whereby the system is pushed into the metastable region at constant pressure *as it is rapidly heated* [4]; clearly, this is incorrect. (ii) Although the possibility of a spinodal decomposition—in the mechanically unstable region below the spinodal curve [2]—cannot be completely excluded, it is unlikely to be responsible for ablation since the voids grow as highly localized perturbations, i.e., bubbles [Fig. 1(b)].

The above scenario, observed across the whole ablated region, confirms that phase explosion is the primary ejection mechanism under *near-adiabatic cooling*

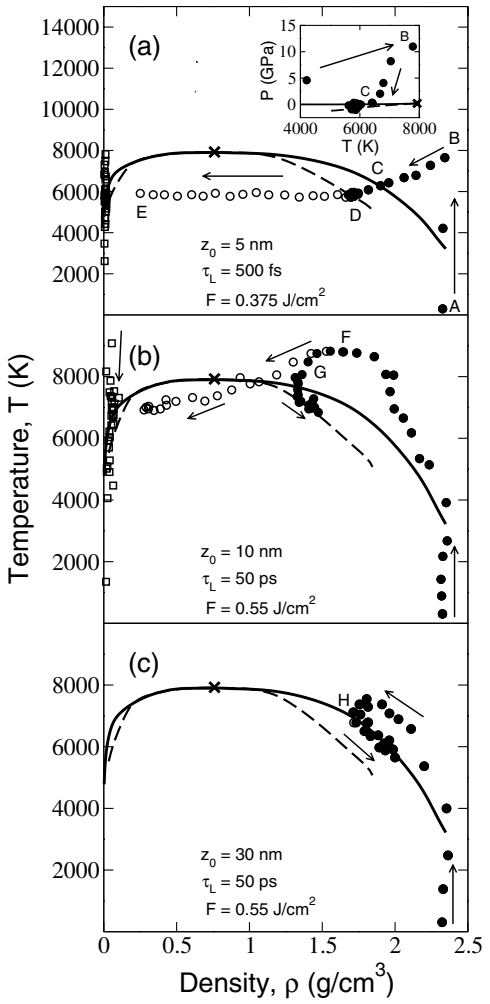

FIG. 2. Time evolution of the system in the ρ-T plane for different pulse durations, fluences, and depths z_0 below the original surface (as indicated). Full circles: dense branch; open circles: macroscopic branch; squares: gas branch. Solid line: binodal [18]; dashed line: spinodal [19]; cross: critical point [19]. Arrows indicate the flow of time.

conditions close to the threshold energy [2,9]; we have obtained similar results for a 5 ps pulse. However, as the pulse duration is increased, i.e., under slower heating conditions, slower expansion and significant thermal diffusion are expected. We show below that this has important consequences for matter removal.

Figure 2(b) displays a typical trajectory for ablation with a 50 ps pulse slightly above the threshold fluence, $F_{\rm th}^b = 0.45$ J/cm^2. As in the case of a fs pulse, heating is fast enough to pull the liquid away from the binodal (where it is in equilibrium with the vapor), thus causing the system to initially evolve above the liquid-gas coexistence region and reach a supercritical state (F). In contrast to fs irradiation, however, significant expansion occurs during the pulse, i.e., heating is nonisochoric. Also, the system does not cross the binodal line in a *homogeneous* state: rather, the split of the dense and macroscopic branches, marking the onset of ablation, takes place *outside* of any phase coexistence region (G). Thus, in this case, matter removal cannot be attributed to phase explosion nor spinodal decomposition. The above behavior has been observed over the *entire* ablated volume above $F_{\rm th}^b$: we have *not* found a single case where the metastable region is accessed in a homogeneous state. Simulations using a two-dimensional Lennard-Jones model for pulse durations of a few tens to a few hundreds of ps corroborate these observations [20].

The breakup of an expanding supercritical fluid during short-pulse laser ablation has recently been attributed to fragmentation [9]. As discussed below, this is proposed as the primary ablation mechanism under *nonadiabatic cooling conditions*. It can be seen as a structural rearrangement of the system into clusters during the expansion caused by the pressure buildup. Two limits must be considered: (i) under fs irradiation, the rapid expansion of the material can be such that the equilibrium structure can no longer be preserved (e.g., by atomic diffusion); (ii) for significantly longer pulses, the equilibrium structure is likely to be maintained during the (slower) expansion. However, because a fluid at sufficiently low densities is in general not homogeneous, its dissociation into fragments is still possible and is referred to as "trivial" fragmentation [10]. In any case, fragmentation should not be confused with spallation whereby the material is brought into the solid-gas coexistence region by strong tensile pressure waves [10].

The dynamics of a homogeneous system cooling towards the liquid-gas regime depends strongly on the rate at which it expands. This is revealed in Fig. 2(c) for a section of the *unablated* material irradiated by a 50 ps pulse. Heating is nonisochoric and, as it cools, the system reaches the binodal (H). The key point is that, although it does so in the same region as for a 500 fs pulse [point C in Fig. 2(a)], the slower expansion allows significant heat diffusion to take place: the system does not enter the metastable region but, rather, cools along the binodal by thermal diffusion. As detailed below, the absence of explosive boiling for sufficiently long pulses is the result of slow material expansion and efficient heat conduction.

Based on these observations, a schematic overview of the thermodynamic pathways to ablation for pulse durations of $\sim 10^{-13}$ to 10^{-8} s emerges as depicted in Fig. 3 and discussed below:

(i) Miotello and Kelly have argued that, for sufficiently short ($\lesssim$1000 ns) pulses, rapid heating pushes the system into the metastable region where homogeneous nucleation of gas bubbles takes place [4]; in the ρ-T plane, this can *conceptually* be represented by K $\rightarrow$ M. If this were so, explosive boiling would be the only mechanism relevant to short-pulse laser ablation.

(ii) The existence of various ablation mechanisms can be understood if one considers, instead, that rapid heating pulls the system *away* from the metastable region; the rate at which expansion proceeds as the material subsequently *cools* is determinant for the ablation process. This is best

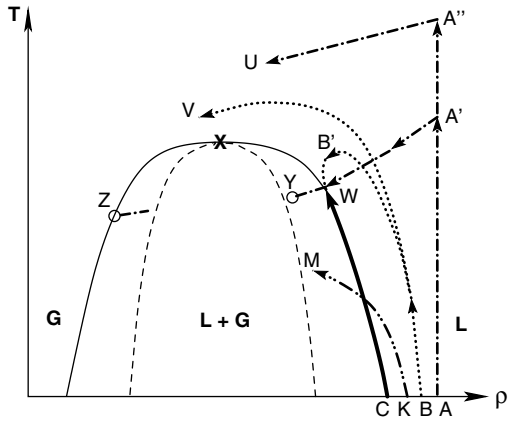

FIG. 3. Thermodynamic trajectories of a hypothetical semiconductor or metal under fs (dashed-dotted line), ps (dotted line), and ns (thick solid line) laser irradiation. Thin solid line: binodal; dashed line: spinodal; cross: critical point. L: liquid; G: gas. Other capital letters refer to locations in the phase diagram (see text).

viewed by considering an arbitrary point of entry into the metastable region along the binodal (W). Under fs irradiation, isochoric heating leads to the buildup of a strong pressure within the material, later released via mechanical expansion. At high energies, the resulting rapid expansion causes the breakup of the supercritical fluid through fragmentation ($A \rightarrow A'' \rightarrow U$) [10]. Closer to the threshold energy, however, the expansion is too slow to induce fragmentation. Nevertheless, it is sufficiently rapid to push the system into the metastable regime (near the spinodal limit) *before significant thermal diffusion has occurred* ($A \rightarrow A' \rightarrow W \rightarrow Y$), i.e., cooling is adiabatic. Homogeneous bubble nucleation then sets in, converting the superheated material into a mixture of liquid and gas ($Y \rightarrow Z$), a first-order transition. Conversely, under irradiation with long (ns) pulses, the material responds to the slow heating with a slow expansion *along* the binodal ($C \rightarrow W$), likely up to the critical point where phase separation proceeds via a second-order transition; for $\tau_L \gtrsim 100$ ns, vaporization may also be important [8].

(iii) Consequently, there must exist a "critical" pulse duration, τ_L^c, beyond which phase explosion is suppressed. This is illustrated by the trajectory $B \rightarrow B' \rightarrow W$ for a pulse of intermediate (ps) duration. Following nonisochoric heating the system cools towards the liquid-gas regime. Here, however, expansion occurs in a time of the order of, or greater than, the characteristic time for heat conduction ($\tau_{\text{th}} \sim 10^{-11}$ s, [21]). As a result, the system cools along the binodal by thermal diffusion, i.e., it does not enter the metastable region and phase explosion does not take place. In this case, only those regions associated to an expansion above the critical point contribute to the ablated mass ($B \rightarrow V$), here through a fragmentation process (trivial or not).

In summary, explosive boiling is particular to ultrashort-pulse laser irradiation where near-isochoric heating conditions lead to a rapid adiabatic cooling of the material. This regime is characterized by (i) the time needed to induce a collective motion of the atoms, $\tau_s = \delta/c_s(\rho)$, where δ $(= 1/\alpha)$ and $c_s(\rho)$ are, respectively, the optical penetration depth and the speed of sound [6]; (ii) the time needed to observe significant thermal diffusion, τ_{th}. With $\delta \sim 10^{-8}$ m (as expected for a *metallic liquid* at the surface of a metal or semiconductor) and $c_s(\rho \approx \rho_0) \sim 10^3$ m/s, this yields a pulse duration upper limit $\tau_L^c \sim \tau_s \sim \tau_{\text{th}} \sim 10^{-11}$ s for phase explosion; τ_L^c could be higher in materials where heat diffusion is slower. For $\tau_L > \tau_L^c$, fragmentation remains the only relevant ablation mechanism.

We are most grateful to D. Perez for fruitful discussions. P. L. also wishes to thank K. Sokolowski-Tinten and D. von der Linde for useful insights. This work has been supported by grants from the Canada's NSERC and Québec's FQRNT. We are indebted to the *Réseau québécois de calcul de haute performance* for generous allocations of computer resources.

*Electronic address: lorazop@MAGELLAN.UMontreal.CA

[1] M. von Allmen and A. Blatter, *Laser-Beam Interactions with Materials* (Springer, Berlin, 1995), 2nd ed.
[2] K. Sokolowski-Tinten *et al.*, Phys. Rev. Lett. **81**, 224 (1998).
[3] D. von der Linde and H. Schüler, J. Opt. Soc. Am. B **13**, 216 (1996).
[4] A. Miotello and R. Kelly, Appl. Phys. Lett. **67**, 3535 (1995).
[5] J. H. Yoo *et al.*, Appl. Phys. Lett. **76**, 783 (2000).
[6] L. V. Zhigilei *et al.*, Chem. Rev. **103**, 321 (2003).
[7] F. Vidal *et al.*, Phys. Rev. Lett. **86**, 2573 (2001).
[8] R. Kelly and A. Miotello, Phys. Rev. E **60**, 2616 (1999).
[9] D. Perez and L. J. Lewis, Phys. Rev. Lett. **89**, 255504 (2002).
[10] D. Perez and L. J. Lewis, Phys. Rev. B **67**, 184102 (2003).
[11] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985).
[12] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, Oxford, 1987).
[13] A. M. Malvezzi, J. M. Liu, and N. Bloembergen, Mater. Res. Soc. Symp. Proc. **23**, 135 (1984).
[14] M. Lundstrom, *Fundamentals of Carrier Transport* (Addison-Wesley, Reading, MA, 1990).
[15] G. L. Eesley, Phys. Rev. B **33**, 2144 (1986).
[16] H. M. van Driel, Phys. Rev. B **35**, 8166 (1987).
[17] V. V. Godlevsky, J. J. Derby, and J. R. Chelikowsky, Phys. Rev. Lett. **81**, 4959 (1998).
[18] N. Honda and Y. Nagasaka, Int. J. Thermophys. **20**, 837 (1999).
[19] D. V. Makhov and L. J. Lewis, Phys. Rev. B **67**, 153202 (2003).
[20] D. Perez and L. J. Lewis (unpublished).
[21] D. von der Linde, K. Sokolowski-Tinten, and J. Bialkowski, Appl. Surf. Sci. **109–110**, 1 (1997).