Simulation of picosecond pulsed laser ablation of silicon: the molecular-dynamics thermal-annealing model

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ABSTRACT

A molecular-dynamics thermal-annealing model (MADTAM) is proposed to study the mechanisms of ablation induced in crystalline silicon by picosecond pulses. In accordance with the thermal annealing model (TAM), a detailed description of the microscopic processes resulting 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. Above the predicted threshold energy for ablation, $F_{th} = 0.25$ J/cm^2, ablation is driven by subsurface superheating effects: intense heating by the pulse leads to the thermal confinement of the laser-deposited energy. As a result, the material is overheated up to its critical (spinodal) point and a strong pressure gradient builds up within the absorbing volume. At the same time, diffusion of the carriers in the bulk leads to the development of a steep temperature gradient below the surface. Matter removal is subsequently triggered by the relaxation the pressure gradient as a large few tens of nm thick piece of material is expelled from the surface.

Keywords: Laser ablation, thermal annealing model, subsurface superheating effects, molecular dynamics, silicon

1. INTRODUCTION

Identification of the mechanisms involved in light-induced matter removal is, undoubtedly, a crucial issue: in laser cutting and drilling of surfaces, achievement of a precise control of the ablated volume by an appropriate choice of the laser parameters would open up new possibilities in laser-assisted tailoring of materials. In pulsed laser deposition of thin films, the ejection of molten micron-sized droplets, i.e. splashing, has impeded the implementation of the technique for large-scale industrial applications.[1,2] A number of solutions have been suggested to limit the size and number of droplets reaching the substrate, but generally without addressing the problem of their formation (see Ref. 2 and references therein).

The ablation processes brought about in metals and organic solids by picosecond pulses have been ascribed, so far, to photothermal and photomechanical effects:[3,4] while the former mechanisms imply a fast transition from a superheated liquid to a mixture of liquid droplets and single atoms or molecules, i.e. a phase explosion, the latter are associated with the build-up and subsequent relaxation of a strong pressure gradient in the bulk; both of these processes have been observed in a recent molecular-dynamics (MD) study of organic solids.[4] There have also been repeated reports of subsurface superheating (SSSH) effects involved in matter removal with light:[5,6] here, evaporation of the surface leads to its rapid cooling, the subsurface region therefore retaining a higher temperature; as a result, a strong pressure develops beneath the surface and ejection of matter proceeds similarly to a phase explosion. However, it is unclear whether this mechanism is real as conflicting views can be found in the literature.[3,5,7]

In semiconductor materials, the processes underlying the ejection of matter by picosecond pulses have yet to be determined. In this paper, a molecular-dynamics thermal-annealing model (MADTAM) is proposed to simulate the interaction of 308 nm, 10 ps, pulses with silicon; this is a continuation of our previous MD study of laser ablation of Si.[8,9] Our simulations suggest matter removal mechanisms driven by SSSH effects. Interestingly, overheating of

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the subsurface region is not, here, the result of a vaporization process at the surface but, rather, a consequence of carriers diffusing into the bulk.

2. THE MODEL

A detailed description of the model can be found elsewhere.[8,10] Briefly, the supercell forms a (100) substrate with approximate dimensions $3 \times 3 \times 60$ nm^3 and which, using periodic boundary conditions, is repeated in the lateral directions (parallel to the upper surface) to recreate the thermal and structural constraints of a macroscopic crystal. In the direction normal to the surface, however, thermalization is ensured by coupling a few monolayers of atoms at the bottom of the supercell to a heat reservoir. The set of Newton's equations of motion have been solved for a total of 31680 atoms with the interatomic forces computed from the Stillinger-Weber (SW)[11] potential. The MD time step was $\Delta t = 0.5$ fs for all simulations (see, e.g., Ref. 12 for a presentation of the MD method).

A 308 nm, 10 ps, Gaussian pulse is simulated by the successive arrival of planes of photons spanning the entire surface of the supercell, the number of which determined by the instantaneous irradiance, and separated in time by an interval ranging from Δt to typically $10 \times \Delta t$. It is straightforward to show,[8,10] at $\lambda = 308$ nm and ~ 300 K, that one-photon interband transitions are at least a 100 times more frequent than two-photon interband transitions. Moreover, free-carrier absorption has been shown[13] to be negligible for $\lambda \leq 1000$ nm. Therefore, one-photon interband transitions are dominant and all other mechanisms can be ignored. The pulse intensity is assumed to decrease exponentially with depth, i.e. according to the Beer-Lambert law. When a photon is absorbed, an electron-hole pair is created and each carrier is given: (1) an initial position to account for its subsequent diffusion into the bulk; (2) an initial kinetic energy determined from an instantaneous Maxwell-Boltzmann distribution at a temperature T_e; this energy is subsequently transferred to the lattice through carrier-phonon scattering.

Depending upon the value of the carrier density, n, the overall relaxation process can follow two different paths:[14,15] if $n < n_c \sim 10^{22}$ cm^{-3}, as it is generally the case with nano and picosecond pulses, thermal processes are involved and the hot carriers relax by emitting optical phonons in a time $\tau_{LO} \sim 1$ ps; this is known as the thermal annealing model (TAM).[16] With femtosecond pulses, on the other hand, n can be in excess of n_c; if so, non-thermal processes are operative as ultrafast melting proceeds within ~ 1 ps by the collapse of the lattice, i.e., *before* significant phonon generation has occurred.[14,17] Because it is not certain whether the SW potential can account for the latter phenomena, care is taken to remain within TAM: pulses have a duration of 10 ps and fluences are chosen such that $n < n_c$. The hot carriers relax through a number of mechanisms following their generation; these are carrier-phonon scattering, carrier diffusion, impact ionization and Auger recombination. It can be shown[8,10] that the only relevant mechanisms in the present context are carrier-phonon scattering and carrier diffusion. In the first of those outcomes, a carrier either emits or absorbs a phonon; the corresponding quantum of energy, $\hbar\omega_0$ (typically ~ 62.6 meV), is then instantaneously given to, or removed from, the lattice in a radius of 5 Å from the carrier according to a spatial Gaussian distribution. Each carrier is also assumed to diffuse in the direction normal to the surface and *away* from it; this is done to account for the carrier density gradient which builds up as a result of the exponentially-decreasing absorption with depth. Here, the carrier equations of motion are solved by computing the carrier ambipolar diffusion coefficient from an expression suggested by Berz *et al.*[18]

3. RESULTS AND DISCUSSION

All simulations were carried out for a single 308 nm, 10 ps, laser pulse. 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. Matter removal is observed for fluences $F \geq F_{th} = 0.25$ J/cm^2. Fig. 1 shows the position (in nm) of the topmost atomic layer, z_{top}, as a function of time; $z_{top} = 0$ corresponds to the initial position of the surface. The pulse begins at $t = 0$ and the initial temperature of the target is ~ 300 K. During the first few ps, a large number of hot electrons and holes are created which, in turn, heat the lattice by scattering with phonons. As a result, the material undergoes an expansion phase; this is seen in Fig. 1. After ~ 27 ps, however, the material has expanded such that its limit for mechanical stability has been reached, and ablation occurs: from a value of ~ 7 nm, z_{top} drops to ~ -35 nm in a few ps; this indicates that matter removal has taken place over a depth $h \sim 35$ nm, a value consistent with experimental data.[19]

Further insight into the mechanisms responsible for ablation is given in Fig. 2. The lattice temperature, T, is first plotted as a function of depth, z, at $t = 10$ ps; as one can see, a steep temperature gradient has developed below the surface: from a value of ~ 2000 K at $z \sim 0$, i.e. $>$ than the bulk melting temperature of silicon, $T_m = 1685$ K,[20] T rises rapidly to reach a plateau slightly above the critical (spinodal) temperature, $T_c = 5193$ K.[20]

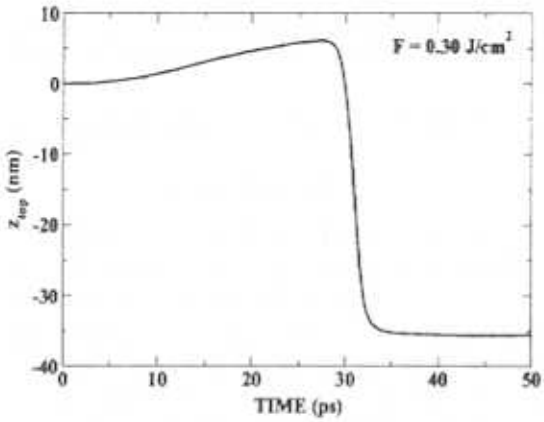

Figure 1. Position of the topmost atomic layer, z_{top}, as a function of time. The fluence is $F = 0.30$ J/cm^2.

Here, the maximum temperature is not located at the surface but, rather, a few tens of nm below it: because of the exponentially-decreasing absorption with depth, more carriers are created near the surface and a carrier density gradient builds up; therefore, the electrons and holes are assumed to diffuse in the direction given by the latter, i.e. *away* from the surface, and a large part of the energy is thus carried into the bulk by the electronic degrees of freedom. In addition, the intense heating by the pulse leads to the thermal confinement of the laser-deposited energy;[10] as a result, 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 gradient develops at $40 \leq z \leq 50$ nm, as shown in Fig. 2b. By $t \sim 21$ ps, the latter has relaxed and led to the development of important tensile stresses in the material; these are responsible for the rapid expansion phase observed for $t > 10$ ps in Fig. 1. Ablation follows as the material can no longer expand: relaxation occurs through the ejection of a large — few tens of nm thick — piece of molten material with an initial velocity component normal to the surface of ~ 1000 m/s.[10]

The phenomena described above, together with the steep temperature gradient, are indicative of important subsurface superheating effects.[3,6] The temperatures involved are too high to be associated with photomechanical effects.[4] Moreover, phase explosion mechanisms require that $\partial T/\partial z \sim 0$, which is not the case here; it should be noted that the temperature gradient in Fig. 2a is not caused by a vaporization process at the surface but, rather, is a consequence of carriers diffusing into the bulk.[10] However, a more precise assessment of the mechanisms involved

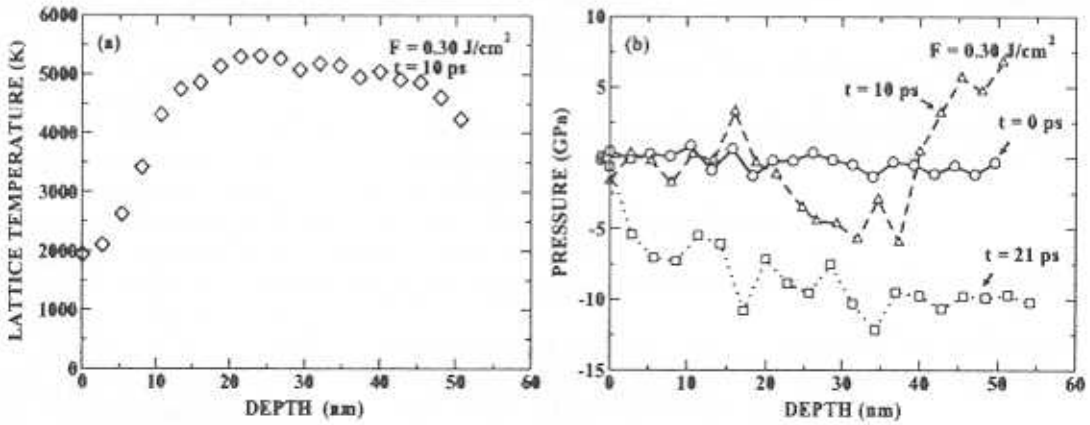

Figure 2. Lattice temperature, T, and pressure, P, as a function of depth, z: (a) T as a function of depth at the end of the pulse, $t = 10$ ps; (b) P as a function of depth at different times. The fluence is $F = 0.30$ J/cm^2.

in the laser ablation of silicon with picosecond pulses suggests the implementation of surface effects; these have been observed in a recent study of hot carrier dynamics at a Si(100) surface.[21] Accounting for surface effects is currently under development.

Full details of the calculations and complete results will be given elsewhere.[10]

4. SUMMARY

A molecular-dynamics thermal-annealing model (MADTAM) has been proposed to study the mechanisms of matter removal brought about by picosecond pulses in silicon. This has been achieved by embedding carrier-phonon scattering and carrier diffusion into a molecular-dynamics scheme.

Above the predicted threshold energy for ablation, $F_{th} = 0.25\ \mathrm{J/cm^2}$, our simulations reveal important subsurface superheating effects: rapid heating by the pulse leads to the the thermal confinement of the deposited energy. As a result, the material is overheated up to its critical (spinodal) point and a strong pressure builds up in the bulk. In addition, diffusion of carriers away from the surface causes a steep temperature gradient to develop within the absorbing volume. Ablation proceeds from the relaxation of the pressure gradient as a few tens of nm thick piece of material is expelled from the surface.

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