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The role of inertial and spatial confinement in laser interaction with organic materials

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ABSTRACT

Short-pulse laser irradiation of organic material performed under conditions of inertial or spatial confinement can result in laser damage or material ejection (ablation) at relatively low laser fluences. A computational investigation of the mechanisms of the efficient transformation of the deposited laser energy into the energy of material ejection is used in this work to discuss a number of potential applications of the regime of confined laser ablation. In particular, we show that a direct irradiation of a bulk organic sample by a laser pulse performed in the regime of stress confinement can lead to the ejection of a layer of a relatively intact material with thickness determined by the laser penetration depth and fluence. Further irradiation of the spalled layer by an intense femtosecond laser pulse leads to efficient emission of picosecond bunches of energetic ions directed toward the target. In another example, a controlled deposition of functional organic molecules into a designated region of a polymer substrate is achieved by laser irradiation of a microscopic amount of molecular substance spatially confined in the tip of a micropipette.

1. INTRODUCTION

The interaction of laser pulses with organic matter can lead to thermal, chemical or mechanical modification of an irradiated target. At high laser fluences, laser irradiation can cause an extensive damage or massive material removal (ablation) from a target. The laser-induced processes in organic materials have been successfully adapted in a number of important practical applications, including laser surgery [1], mass spectrometry of large non-volatile biomolecules [2], surface microfabrication of polymer thin films [3], and manufacturing of electronic devices [4,5]. A complete understanding of the laser-induced processes is required for optimization of experimental parameters in current applications and for design of new laser processing techniques.

The effect of laser irradiation of an organic material is normally associated with photochemical reactions or thermal processes such as melting, evaporation and boiling. At the same time, it has been predicted by computer simulations [6,7,8] and observed in experiments [9,10] that a short-pulse laser irradiation can cause a massive material removal or laser damage at energy densities much lower than those required for boiling and vaporization. A plausible explanation for the onset of "cold" laser ablation has been proposed based on consideration of photomechanical effects caused by laser-induced stresses [6,7,8,9,10,11]. It has been discussed that the magnitude of the laser induced stresses and the role of the associated photomechanical effects in material removal becomes significant when the laser pulse duration, τ_p, is shorter then the time of mechanical equilibration of the absorbing volume, τ_s. This condition, usually referred as inertial or stress confinement, can be expressed as $\tau_p \leq \tau_s \sim L_p/C_s$, where C_s is the speed of sound in the irradiated material and L_p is the laser penetration depth. Mechanical or spatial confinement of an absorbing material can also contribute to the build up of high compressive pressure, leading to a forwarded ejection of the organic material [12,13] or generation of strong pressure waves in the sample [14].

In this paper we discuss the effects of inertial and spatial confinement based on the results of computational investigation of specific systems that have important potential applications. One series of simulations is used to investigate the effect of spallation of a layer of a bulk organic sample by pulsed laser irradiation performed in the regime of inertial stress confinement. Another series of simulations is performed to study the mechanisms of molecular transfer from a micropipette irradiated by a

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short laser pulse into a sub-micron region of a polymer surface. A short review of computational methods used in simulations of laser-induced processes in organic materials is given bellow and is followed by the discussion of the simulation results for the two systems.

2. COMPUTATIONAL METHODS

Recent progress in understanding many aspects of laser ablation of organic materials has been expedited by the development of advanced computational methods and their application to various processes induced by pulsed laser irradiation. In particular, a molecular-level breathing sphere model [15] has yielded a wealth of information on the microscopic mechanisms of laser ablation, parameters of the ejected plume (velocity distributions, cluster size distributions) and their dependence on the irradiation conditions (laser fluence, pulse duration, initial temperature of the sample) [6,7,16,17]. At smaller time- and length-scales, conventional atomic-level molecular dynamics simulations have demonstrated the ability of this technique to provide detailed information on the dynamics of intermolecular redistribution of the deposited laser energy [18,19]. At the level of the plume expansion, Direct Simulation Monte Carlo method has been shown to be suitable for realistic simulations of the multi-component ablation plume development on the time- and length-scales of a real experimental configuration [20,21]. Finally, the multi-component collisional electromagnetic particle-in-cell method has been successfully used in simulations of the dynamics of solid density plasmas created by ultra-short femtosecond laser pulses [8,22].

The simulations discussed in the present paper are performed using the breathing sphere model that has been developed for molecular dynamics simulations of laser-induced processes in molecular systems. The model assumes that each molecule (or an appropriate group of atoms) can be represented by a single particle that has the true translational degrees of freedom but an approximate internal degree of freedom. This internal (breathing) mode allows one to reproduce a realistic rate of the conversion of internal energy of the molecules excited by the laser to the translational motion of the other molecules. Since the molecules rather than the atoms are the particles of interest in the model, the system size can be large enough to model the collective dynamics leading to laser ablation and damage. Moreover, since we are not following high frequency atomic vibrations, we can use a much longer timestep in the numerical integration and keep track of the processes in the simulated system for a longer time. A more detailed description of the model is given elsewhere [15,17].

3. INERTIAL CONFINEMENT: LASER SPALLATION OF A SURFACE LAYER

An extensive computational study of laser ablation has revealed a strong dependence of the character of the processes leading to the material ejection on the laser pulse duration [6,7,8]. With longer laser pulses, in the regime of thermal confinement, phase explosion of the overheated material leads to the ejection of liquid droplets and gas phase molecules. With shorter pulses or larger penetration depths there is stress confinement and high thermoelastic pressure can cause mechanical fracture or spallation. In this case material disintegration is localized within the spallation region leading to the onset of massive material removal at lower laser fluences and to ejection of larger and colder molecular clusters as compared to the ablation in the regime of thermal confinement. The energetically efficient laser ablation predicted by the calculations can be related experimental observations suggesting that short-pulse laser ablation can be initiated at the energy densities much lower than those required for boiling and vaporization [9,10]. Moreover, observations from scattering experiments for laser ablation of polymer targets by Hare *et al*. [23] suggest that photomechanical effects in the regime of stress confinement can lead to the ejection of a relatively intact layer of material that maintains its integrity at least on the timescale of tens of nanosecond.

The dynamics and microscopic mechanisms of laser-induced spallation can be discussed based on the results of a molecular dynamics simulation of laser irradiation of a molecular solid performed at a laser fluence of 31 J/m^2, a pulse duration of 15 ps, and a laser penetration depth of 50 nm. Snapshots from this simulation are shown in Figure 1. In this simulation we observe that shortly after the end of the laser pulse a few voids are nucleated at a certain depth under the irradiated surface. The snapshots taken at 100 ps, 200 ps, and 500 ps show a fast growth of one of the voids that eventually leads to the separation of a large surface layer from the bulk of the sample, as shown by the snapshot at 1000 ps. The number of molecules in the ejected layer corresponds to the 16 nm layer of the original sample. By 1 ns the layer is located at 50 nm above the original surface of the target and is moving from the target with a velocity of 16 m/s. The density of the gas phase molecules between the layer and the remaining target is ~1.5x10^{19} molecules/cm^3 which is less than the density of an ideal gas under normal conditions. The velocity of the layer, therefore, will not be affected by the expansion of the gas phase and will remain constant at later times. The average temperature of the layer is 726 K, a value below the melting temperature of the model material, 750 K. An

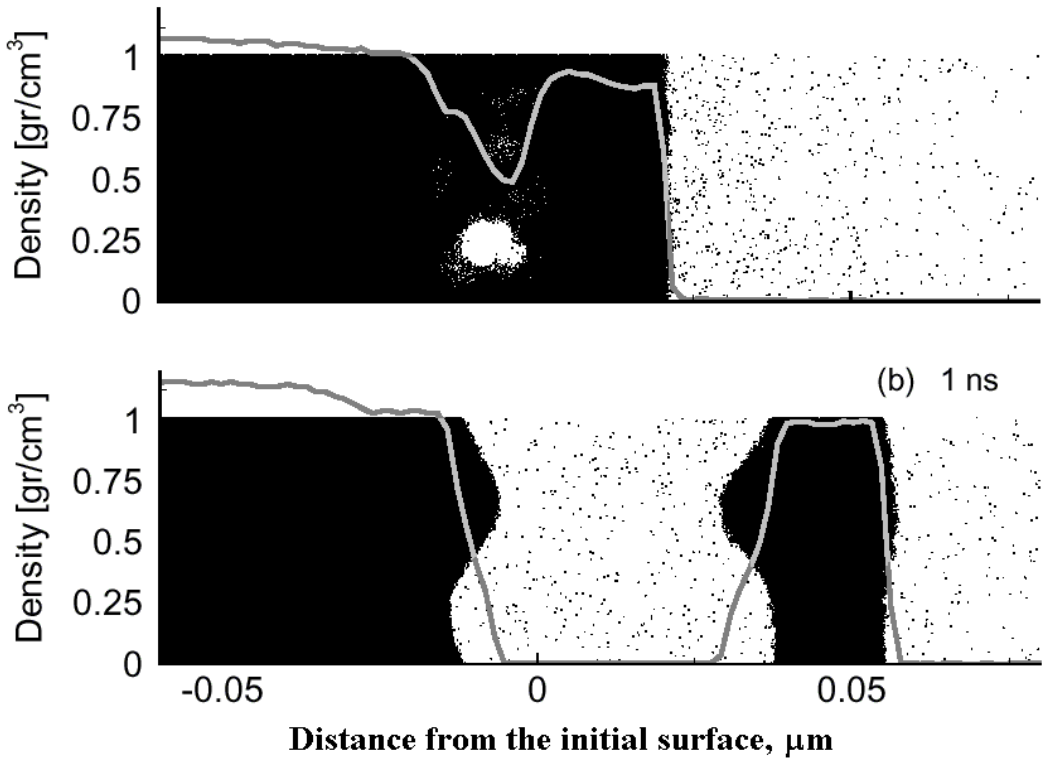

Figure 1. Density profiles and corresponding snapshots for simulation of laser ablation of a molecular solid with a 15 ps laser pulse and a fluence of 31 J/m^2.

apparent viscous, liquid-like behavior observed in Figure 1 can be explained by the tensile stresses in the region of void formation that can locally reduce the melting temperature of the material.

It is evident from the low temperature of the ejected layer and from the visual analysis of the snapshots given in Figure 1 that the physical processes leading to the material ejection have a mechanical rather than thermal character. We find that the

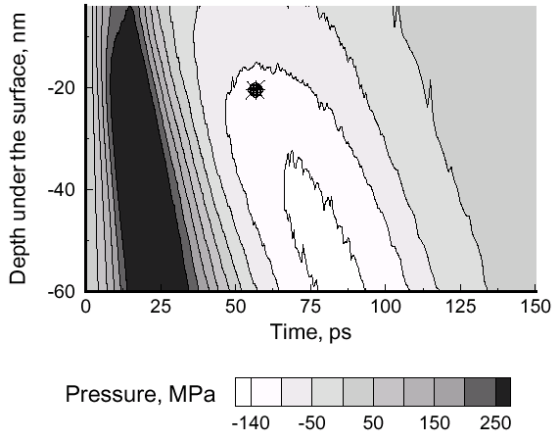

Figure 2. Pressure contour plot for simulation of 15 ps laser pulse irradiation of a molecular sample.

condition of stress confinement, realized in the present simulations, results in the buildup of a high pressure within the absorbing region during the laser pulse. The pressure buildup can be seen in Figure 2, where the spatial and time development of the local hydrostatic pressure in the irradiated sample is shown in the form of a contour plot. Interaction of the laser induced pressure with the free surface leads to the development of the tensile component of the pressure wave propagating from the irradiated surface. The tensile stresses exceed the dynamic tensile strength of the material at a certain depth under the surface and causees mechanical fracture or spallation. The microscopic mechanism of spallation observed in the simulations and consisting of nucleation, growth and coalescence of voids is in a qualitative agreement with a recent theoretical model proposed in Ref. [24] for the spallation at high strain rates.

For simulations performed in the stress confinement irradiation regime the spallation of a surface layer of the sample is found to be the dominant process of laser ablation in a relatively wide range of fluences, from ~29 J/m^2 up to ~35 J/m^2. At higher laser fluences the ejected material decomposes into liquid droplets and individual molecules with the fraction and the average size of the droplets decreasing

with fluence. In the simulations performed with longer, 150 ps pulses, when the stress confinement condition is not satisfied, the photomechanical effects do not play any significant role in the material ejection and no layer spallation is observed at any fluence [7].

Recent computational results [8] suggest a potential application of the laser-induced spallation for an efficient generation of energetic ions directed towards the target sample. It has been demonstrated that the irradiation of the spalled layer by an intensive femtosecond laser pulse can lead to an efficient emission of ions with energies over 1 MeV. Energetic ions produced in the proposed two-pulse experimental setup can be adopted for ion accelerators or used directly in various applications ranging from materials physics and chemistry to nuclear physics.

4. SPATIAL CONFINEMENT: NANO-JET EJECTION FROM A MICROPIPETTE

In additional to the inertial confinement, a mechanical spatial confinement of the absorbing material can contribute to the high pressure buildup and high velocities of the ejected material. The effect of spatially confined ablation has been successfully adopted in the novel techniques for molecular implantation proposed recently by Goto et al. [12,13]. In this technique, a controlled deposition of organic molecules into a designated region of a polymer substrate is achieved by laser irradiation of a microscopic amount of molecular substance spatially confined in the tip of a micropipette. Experimental exploration of this technique has revealed a strong fluence dependence of the molecular ejection process and hence the final state of the molecular material deposition at the substrate. Three distinct regimes have been identified. At laser fluences below a certain threshold fluence no signs of implantation or molecular transfer to the substrate is observed. Just above the threshold fluence, formation of a well-defined molecular cluster at the surface of the polymer substrate has been observed. No implantation into the

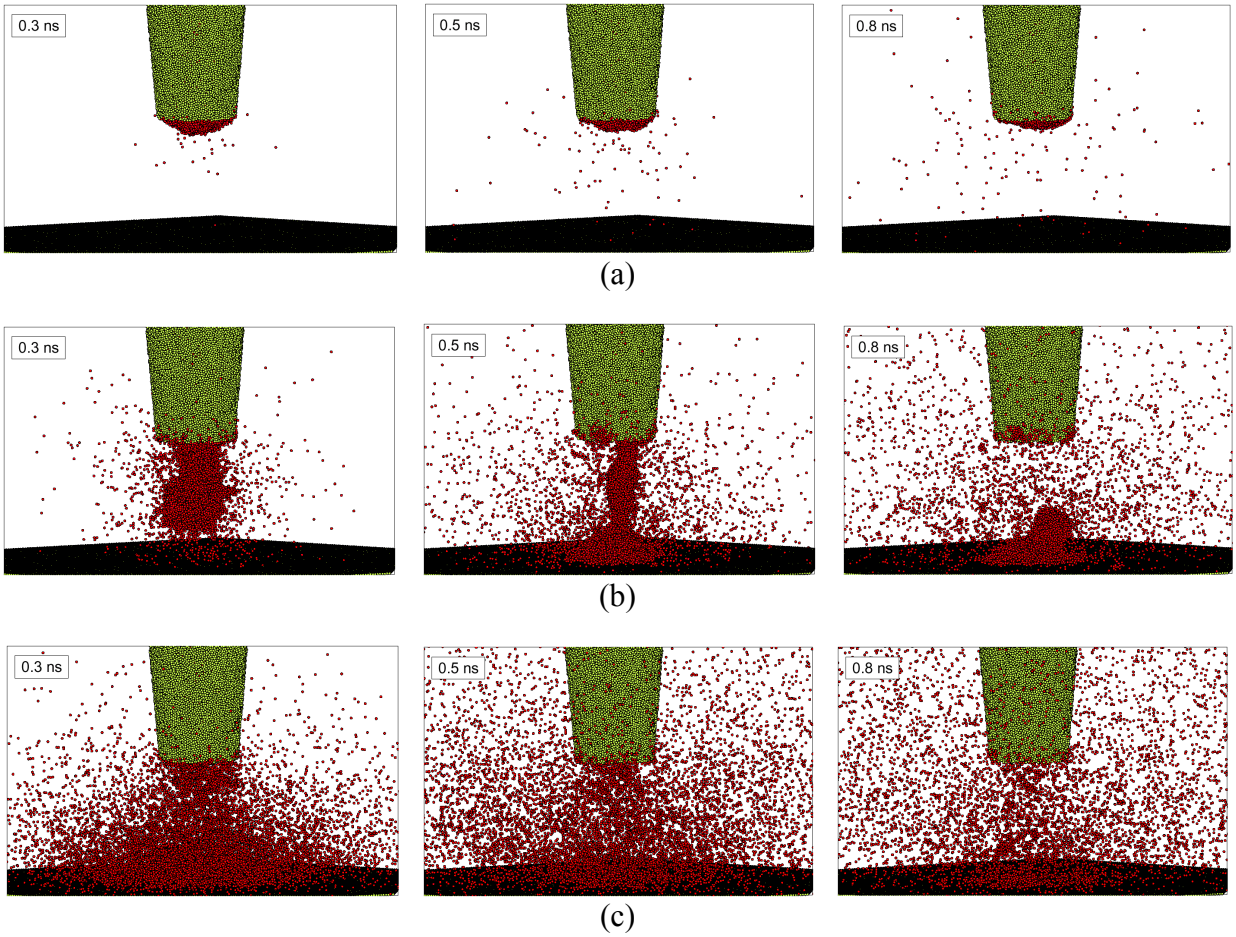

Figure 3. Snapshots from the simulations of molecular ejection from an irradiated pipette tip. The laser pulse duration is 100 ps, the energy density deposited by the laser pulse are (a) 0.2 eV/molecule, (b) 0.4 eV/molecule, (c) 0.8 eV/molecule.

polymer substrate is observed in this regime and the cluster can be moved around the substrate with an AFM tip. At higher laser fluences an efficient implantation of the ejected molecules into a sub-micron region of the substrate is observed.

In order to get a qualitative understanding of the processes leading to the implantation or cluster deposition, we perform a series of simulations of molecular ejection from a doped nano-pipette [25]. The simulations are performed using the breathing sphere model that has been adapted to match the experimental system. The parameters of the intermolecular potential in the breathing sphere model are chosen to reproduce density and the melting point of coumarin 545 (C545) molecular solid and a mass of 374 Daltons is attributed to each molecule. Molecular material is located in the tip of a rigid pipette and the pipette is positioned 45 nm above the substrate. The size of the pipette and the pulse duration are scaled down in order to reduce computational time. The opening of the pipette tip of 28 nm and the laser pulse duration of 100 ps are chosen in order to make sure we are in the same physical regime of thermal confinement as in experiments. The pulse duration of 100 ps is longer than the time required for the relaxation of the laser-induced thermo-elastic stresses and the photomechanical effects do not play any significant role in the material ejection in the simulations as well as in the experiments. The laser irradiation at a wavelength of 500 nm (2.48 eV) is modeled by vibrational excitation of molecules that are randomly chosen during the laser pulse duration among the molecules located in the pipette tip.

The snapshots from the simulations at three different laser fluences are shown in Figure 3. A visual inspection of the snapshots reveals a strong fluence dependence of the molecular ejection process and the final state of the molecular material deposited on the substrate. We find that at low laser fluences molecular material melts inside the tip and a small number of molecular monomers is ejected, Figure 3a. As fluence increases, the temperature of the molecular material in the tip increases above the boiling point leading to the release of the gas phase molecules and expulsion of the liquid droplet from the tip, Figure 3b. In this simulation the bulk part of the ejected material forms a compact liquid droplet on the substrate. Fast cooling of the droplet due to the evaporation and heat conduction to the substrate leads to the formation of a compact nano-cluster such as the one observed experimentally at sub-implantation fluences. An additional increase of laser fluence leads to a stronger overheating and explosive boiling of the molecular material in the pipette tip. A hot mixture of gas-phase molecules and small clusters is ejected from the tip at these high fluences as shown in Figure 3c. Although we do not simulate implantation step in this work and the substrate is represented by a rigid molecular monolayer, we can speculate that the high temperature of the ejected material and the high ejection velocities (up to 1000 m/s in the front of the ejecta) would lead to the melting and efficient implantation/mixing of the exposed polymer surface region and the dopant molecules. The sub-micron size of the implanted dot observed in experiments is explicable considering the simulation in Figure 3c, which shows that a large area of the polymer substrate is exposed to the hot and mainly gaseous material.

5. SUMMARY

The results of computational investigation presented in this paper demonstrate that short-pulse laser irradiation of organic material performed under conditions of inertial or spatial confinement can result in laser damage or ablation at relatively low laser fluences. The efficient transformation of the deposited laser energy into the energy of material ejection has a number of potential applications. In particular, we demonstrate that a direct irradiation of a bulk organic sample by a laser pulse performed in the regime of stress confinement can lead to the ejection of a layer of a relatively intact material. The results of recent computational study suggest that the effect of laser-induced spallation can be utilized for an efficient generation of energetic ions directed towards the target. In another example, a controlled deposition of organic molecules into a polymer substrate is achieved by laser irradiation of a microscopic amount of molecular substance spatially confined in the tip of a micropipette. This method of ablation confinement, investigated computationally in this work, gives fine spatial control in implantation of functional organic molecules into a designated region of an organic substrate and has potential applications in opto-electronics, drug delivery, and biotechnology.

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