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Y.G. YINGLING
P.F. CONFORTI
B.J. GARRISON✉

Theoretical investigation of laser pulse width dependence in a thermal confinement regime

152 Davey Laboratory, Department of Chemistry The Pennsylvania State University, University Park, PA 16802, USA

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ABSTRACT Previous molecular dynamics (MD) simulations of ultraviolet (UV) laser ablation demonstrate the distinct dependence of material ejection on laser fluence and laser pulse duration. In this paper, we examine the pulse width dependence when the laser pulse widths are appropriate for the thermal confinement regime. We perform MD simulations of laser ablation with a laser pulse duration of 1 ns and compare with a pulse width of 150 ps as in previous simulations. The simulations confirm that the pulse width in thermal confinement regime does not dramatically influence the molecular ejection mechanism. The simulations reveal differentiations, however, in plume composition and the ablation threshold value.

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1 Introduction

Laser ablation has been shown to be important in such applications as laser surgery [1, 2], matrix-assisted laser desorption/ionization (MALDI) [3, 4], surface microfabrication [5, 6], and pulsed laser deposition (PLD) of organic films and coatings [7–10]. The optimization of applications depends on a complete understanding of the underlying processes in laser ablation.

Molecular dynamics (MD) simulations have been shown to provide a microscopic picture of processes involved in laser ablation [11–17]. Previous molecular dynamics (MD) studies by our group have shown the laser pulse width and fluence influence on molecular yield [11, 12], temperature, pressure, energy distributions of ejected molecules, and the state of the remaining target [13, 14]. In previous simulations a 150 ps pulse width was used for simulations in the thermal confinement regime. Laser pulse durations used in UV MALDI sources, however, range from 0.55 ns to 20 ns. In this paper, we examine the question of whether the laser pulse duration in the thermal confinement regime influences the material ejection mechanism. MD simulations are performed using laser pulses of 150 ps and 1 ns.

✉ Fax: 1-814/863-5319, E-mail: bjg@psu.edu

2 Computational setup

The laser ablation process is modeled using a coarse-grained breathing sphere model which is described elsewhere [11–16]. Laser irradiation at a wavelength of 337 nm (3.68 eV) is simulated by random vibrational excitation of molecules. The absorption probability with depth follows Beer's Law with a 50 nm penetration depth [11]. Laser pulse widths of 150 ps and 1 ns are used. Both pulse durations are in the regime of thermal confinement where the pulse is short relative to the characteristic thermal diffusion time across the absorption depth [12]. A computational cell of $10 \times 10 \times 180$ nm (126 950 molecules) is used with periodic boundary conditions implemented on the sides and non-reflecting boundary conditions applied on the bottom of the computational cell. The simulations were performed at fluences of 61 J/m^2 and 100 J/m^2 both of which are above the ablation threshold. To ensure complete material removal, the simulations were carried out for 1 ns (150 ps pulse) and 5.2 ns (1 ns pulse) simulation times.

3 Results and discussion

First we compare simulations with 150 ps and 1 ns pulses operating at the same fluence of 61 J/m^2. In the case of the 1 ns pulse the yield is about 9000 particles, whereas the yield in the case of the 150 ps pulse is 17 000 particles. Examination of the plume composition from simulations of 1 ns irradiation reveals that the plume consists of monomers and slow moving big clusters (Fig. 1). As has been learned from our previous simulations, the ejection of big molecular clusters are expected near the ablation threshold [16]. Moreover, the plume near the ablation threshold exhibits mainly large clusters and monomers. Therefore, we can conclude that the 61 J/m^2 fluence with the 1 ns irradiation is just above the ablation threshold. For the 150 ps laser pulse simulations the ablation threshold was detected at 37 J/m^2 with a yield of 8000 particles [13]. The fluence of 37 J/m^2 with 1 ns irradiation is in the desorption regime of material removal. Hence, the threshold fluence is higher for irradiation with the 1 ns pulse compared with the 150 ps pulse irradiation. The ablation regime is defined by the critical energy density sufficient for the overheating of the surface layer up to the limit of its thermodynamic stability. At the threshold fluence a critical energy

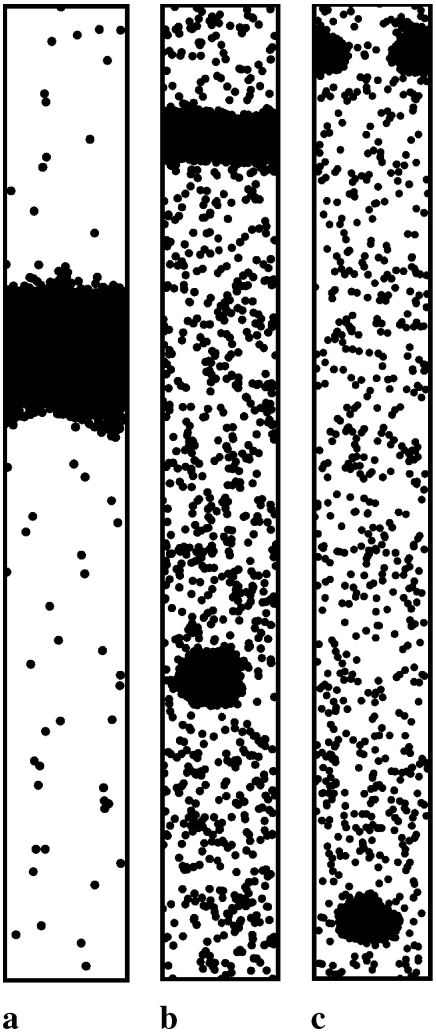

FIGURE 1 Snapshots of a 100 nm slab of the plume for **a** 1 ns pulse and fluence of 61 J/m^2, **b** 150 ps pulse and fluence of 61 J/m^2, and **c** 1 ns pulse and fluence of 100 J/m^2

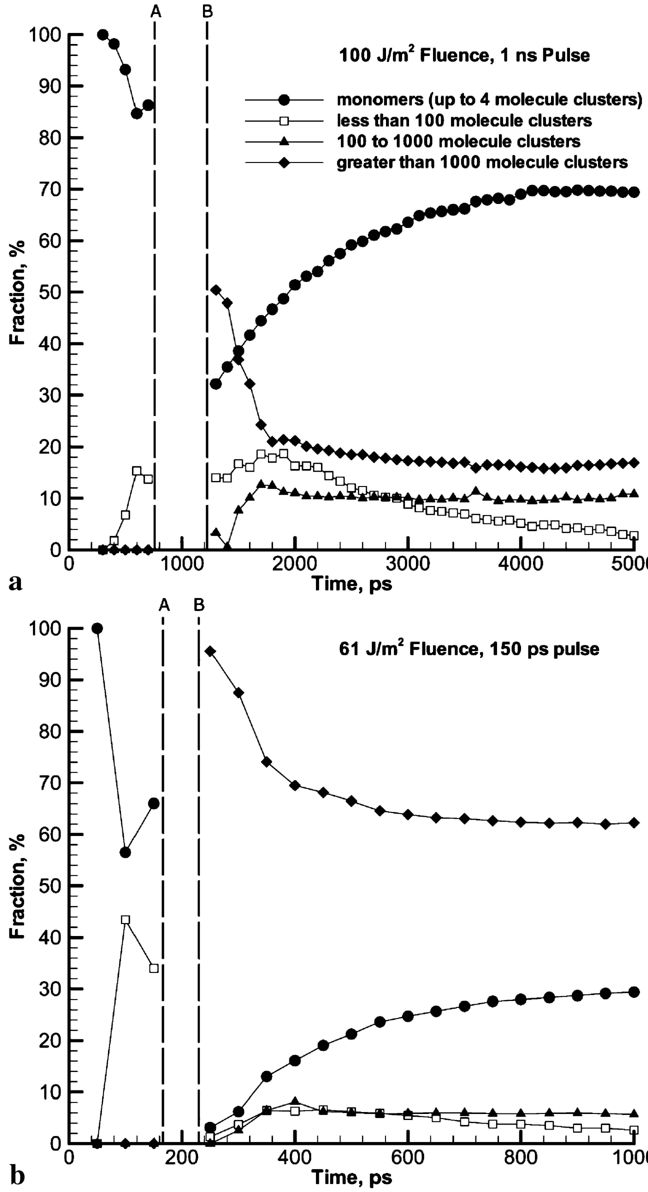

FIGURE 2 The temporal plume composition versus time for **a** 1 ns pulse and fluence of 100 J/m^2, and **b** 150 ps pulse and fluence of 61 J/m^2. Data are not available at times between A and B due to the phase explosion

density is reached in the surface layer [12]. The radial (parallel to the surface) velocity component can be used as a measure of temperature in the surface layer. The temporal radial temperature profiles of the surface layer at the threshold fluence for 1 ns irradiation and 150 ps irradiation are very similar and exhibit the same maximum temperature of 1100 K reached in the surface layer at the end of the laser pulse. The slower heating rate for the 1 ns laser pulse, however, leads to evaporation from the surface and thermal conduction into the bulk of the sample during the laser pulse, which in turn leads to some cooling of the surface layer. Therefore, since more energy drains out of the system during the longer pulses, greater fluences are needed for the onset of ablation.

The differences in the mechanisms of material ejection can be reflected in the parameters of the ablation process. In order to compare the plume characteristics for 1 ns and 150 ps pulse durations, we increased the 1 ns pulse fluence up to 100 J/m^2. Now the molecular yields are similar for the 1 ns pulse simulation at 100 J/m^2 and for the 150 ps pulse simulation at 61 J/m^2 and the snapshots of the plume (Fig. 1b and c) reveal a range of clusters and monomers. The change in the shape and amplitude of the pressure wave can serve as an indicator for the change in the ablation mechanism. For both pulse durations the amplitudes and the shapes of the acoustic pressure wave propagating toward the bottom of the sample are very similar, signifying no basic change in the ejection mechanism. Also, a comparison analysis of the plume characteristics show that the axial and radial velocity distributions for both pulse durations are very similar and are defined by a Maxwell–Boltzmann distribution with a range of flow velocities in the axial direction [14].

The main difference between the two plumes at different pulse durations is the relative contribution of monomers and large clusters. Figure 2 exhibits plume composition versus time for the 1 ns pulse duration (a) and the 150 ps pulse duration (b) simulations. By examining the detailed plume composition we have found that the fraction of monomers in the plume is much greater for 1 ns irradiation than for

150 ps irradiation. During the laser pulse, before the time marked A, a majority of the ejected molecules are monomers which essentially undergo intensive evaporation as the material expands. From times A to B the surface is not defined since there is a transient structure consisting of interconnected liquid clusters and individual molecules which have been ejected from a portion of the original sample. After time B the transient structure decomposes into individual monomers and well-defined clusters. As the cluster fraction decreases the monomer fraction increases due to evaporation of monomers from the surface of the clusters. The description of the molecular ejection, with the decomposition of the ejected material into monomers and clusters, is consistent with the vaporization mechanism predicted from classical thermodynamics [18, 19].

The experimental study by Dreisewerd [20] on the effect of the laser pulse width in MALDI by comparing lasers (337 nm) with 0.55 and 3 ns pulse widths showed that the rate of energy deposition does not play a major role in the desorption/ionization process.

4 Conclusions

The results of our MD simulations show similarities in both pressure and energy characteristics of ablation for the laser pulses of 150 ps and 1 ns. A characteristic phase explosion of overheated material is present at both laser pulse widths, indicating the same molecular removal mechanism. The simulations reveal, however, that the longer laser pulse increases the threshold value and the fraction of monomers in the plume.

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