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Computational and experimental study of the cluster size distribution in MAPLE

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Abstract

A combined experimental and computational study is performed to investigate the origin and characteristics of the surface features observed in SEM images of thin polymer films deposited in matrix-assisted pulsed laser evaporation (MAPLE). Analysis of high-resolution SEM images of surface morphologies of the films deposited at different fluences reveals that the mass distributions of the surface features can be well described by a power-law, $Y(N) \propto N^{-t}$, with exponent $-t \approx -1.6$. Molecular dynamic simulations of the MAPLE process predict a similar size distribution for large clusters observed in the ablation plume. A weak dependence of the cluster size distributions on fluence and target composition suggests that the power-law cluster size distribution may be a general characteristic of the ablation plume generated as a result of an explosive decomposition of a target region overheated above the limit of its thermodynamic stability. Based on the simulation results, we suggest that the ejection of large matrix-polymer clusters, followed by evaporation of the volatile matrix, is responsible for the formation of the surface features observed in the polymer films deposited in MAPLE experiments.
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Matrix-assisted pulsed laser evaporation (MAPLE) is a technique developed with an intention of achieving a soft molecule-by-molecule deposition of high-quality ultra-thin organic films [1,2]. MAPLE targets are typically prepared by dissolving the polymer material to be deposited in a volatile solvent, freezing the homogeneous dilute solution (0.1–5 wt.%) and placing it into a vacuum chamber for deposition. Short pulse laser irradiation of the target results in ablation of the matrix which entrains the polymer molecules along into the plume. The ejected polymer molecules are deposited on a substrate, whereas the volatile solvent molecules are pumped away from the deposition chamber. Although the polymer molecules are dissolved in a MAPLE target down to the molecular level and the entrainment of the polymer molecules in the expanding plume of the volatile matrix does not provide an environment suitable for condensation of polymer clusters, a number of recent investigations of surface morphology of the deposited films reveal an unexpected presence of large surface features [3–5]. The surface features, observed for a wide range of laser fluences, can only be explained by the formation of clusters in the process of the material ejection and deposition of large polymer clusters/droplets to the substrate [6]. In this paper, we report the results of a combined experimental and computational study of cluster ejection and deposition in MAPLE. Cluster size distributions are investigated based on the scanning electron microscope (SEM) imaging of the deposited films and the analysis of clusters ejected from the target in molecular dynamics (MD) simulations of MAPLE. The experimental setup and the results of the SEM analysis of the deposited films are presented first, followed by the description of the computational model and the simulation results.

For the experimental study, MAPLE targets containing 5 wt% of poly(methyl methacrylate) (PMMA) dissolved in toluene are prepared by ultrasonication and flash freezing in liquid nitrogen for 300 s (melting temperature of toluene is ~178 K). Toluene is selected as the matrix solvent due to both its high absorption in the UV and its dissolution characteristics.

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Depositions are performed to p-type single-crystal Si substrates placed at a distance of 7 cm from the target. The chamber is pumped down to a base pressure of 2×10^{-5} Torr prior to the deposition. The laser fluence is varied from 0.045 to 0.75 J/cm^2 using a pulsed excimer laser [$\lambda = 248$ nm, 25 ns full width at half maximum (FWHM)] operating at a frequency of 5 Hz. The morphologies of the deposited films are characterized using a JEOL 6700 SEM.

High-resolution SEM images of the deposited films are used to determine the mass distribution of particles responsible for the formation of surface features. The method used in the evaluation of the particle mass distribution is illustrated in Fig. 1a and b. For each film, a representative area of 0.01 mm^2 is chosen. All the identifiable surface features are then analyzed and the areas of all the features are measured on top-view SEM images, Fig. 1a. Then, a careful analysis of tilted high-resolution SEM images of a number of representative surface features is used to estimate average heights of the surface features of different sizes, Fig. 1b. A linear dependence of the

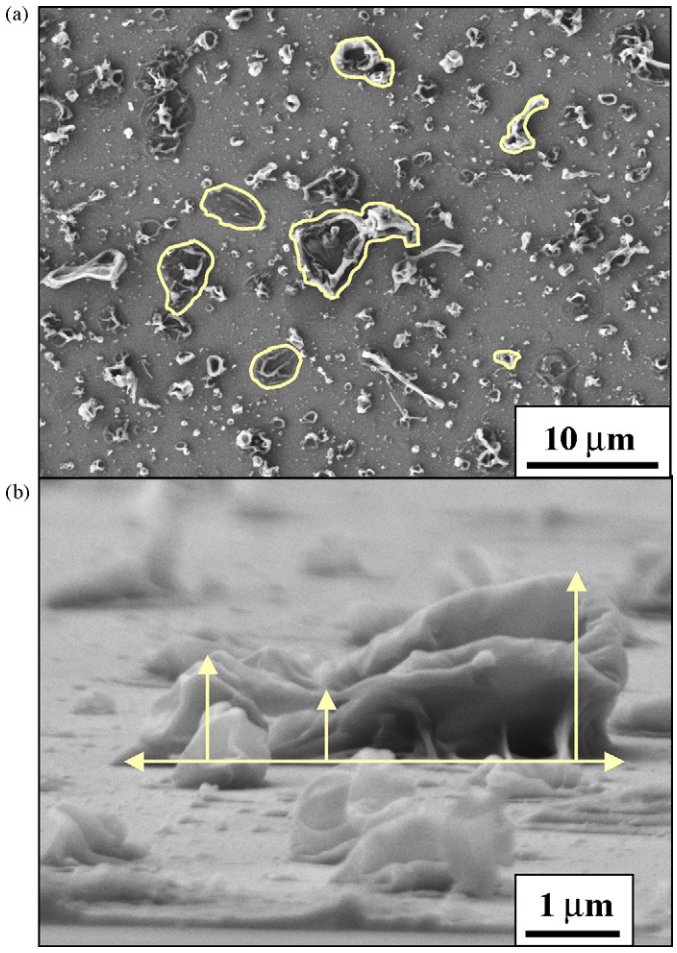

Fig. 1. SEM images of a substrate after MAPLE deposition from a target containing 5 wt.% PMMA in toluene matrix. Experiment is performed with a fluence of 0.13 J/cm^2. Yellow contours in the top view (a) illustrate the method used to evaluate the areas of the surface features. Yellow arrows in the tilted SEM image (b) schematically illustrate the method used to estimate average heights of surface features of different sizes. The areas and heights of surface features are used in estimation of the mass of the deposited polymer droplets, as explained in the text.

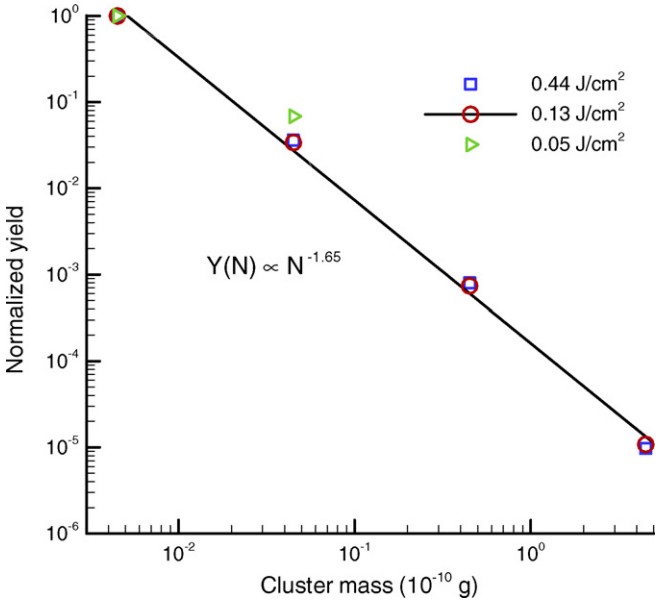

Fig. 2. Normalized mass distribution of particles deposited in MAPLE at fluences of 0.05, 0.13 and 0.44 J/cm^2. The threshold fluence for deposition of polymer particles is 0.045 J/cm^2. MAPLE target is 5 wt.% PMMA solution in toluene. A power-law dependence, $Y(N) \propto N^{-1.65}$, where N represents the mass of the deposited particle, describes well the results for large surface features obtained at all three laser fluences.

average height on the top-view area is found to provide a good description of the results of the measurements. The top-view areas are then converted to volumes using the size-dependent conversion factor. Finally, the masses of the surface features are calculated using the density value for PMMA provided by the manufacturer.

The plot pictured in Fig. 2 shows the normalized yield of deposited particles as a function of cluster mass for three films deposited at fluences of 0.44, 0.13 and 0.05 J/cm^2. The threshold for laser ablation of PMMA/toluene system (and for the polymer film deposition) lies around 0.045 J/cm^2. The mass distribution of the surface features can be described by a power-law dependence, $Y(N) \propto N^{-t}$, where N represents the mass of a surface feature. The same power-law exponent of -1.6, obtained from the fit of the data points for fluence of 0.13 J/cm^2, provides a good description of the distributions plotted for higher, 0.44 J/cm^2, and lower, 0.05 J/cm^2, fluences. The similarity of the three distributions suggests that the mass distribution of the deposited particles has a weak dependence on laser fluence for fluences up to 10 times the ablation threshold.

In order to explain the experimental observations and to reveal the processes responsible for the formation of the large polymer aggregates with complex morphologies, we perform a series of molecular-level computer simulations of the early stages of laser ablation of frozen polymer solutions. The laser-driven material ejection from the target is described by a coarse-grained molecular dynamics model built around the "breathing sphere" model [7]. The model has been actively used for investigation of laser interactions with molecular targets [8]. It adapts a coarse-grained representation of the

molecules by particles with real translational degrees of freedom, but approximate representation of the internal degrees of freedom. The model is capable of describing molecular excitation by laser irradiation, intermolecular energy transfer, as well as the collective molecular dynamics induced by laser irradiation. The polymer molecules are represented by the bead-and-spring model, commonly used in polymer modeling [9]. The ''beads'' representing functional groups of a polymer molecule (monomers) are connected by anharmonic springs with strengths appropriate for chemical bonding. The chains can dissociate if the local forces applied to the chemical bonds are sufficiently large. Intermolecular (non-chemical) interactions among the matrix and polymer molecules are described by a potential chosen to represent the van der Waals interaction in a molecular system [7,8].

The Morse potential defined as $U(l) = E_b(e^{-2\alpha(l-l_0)} - 2e^{-\alpha(l-l_0)})$ is used to represent the intramolecular ''springs'' and intermolecular interactions, both defined as functions of the distance between the edges of the ''breathing spheres'' or polymer ''beads,'' l. For intermolecular interactions, parameters of the potential are given in Refs. [7,8], whereas the following set of parameters is chosen for ''springs'' in the bead-and-spring model based on experimental characteristics of carbon–carbon bonds in polymer molecules: $l_0 = 1.54$ Å, $E_b = 3.48$ eV, and $\alpha = 2.37$ Å^{-1}. The radius of each ''bead'' in the polymer bead-and-spring model is kept fixed during the simulation and is the same as the equilibrium radius of a ''breathing sphere,'' 1.40 Å.

Simulations of laser ablation of polymer-matrix targets are performed at seven laser fluences from 3 to 9 mJ/cm^2 and a concentration of polymer molecules in the MAPLE target of 6 wt.%. The laser pulse duration is 50 ps and the optical penetration depth in pure matrix is 50 nm. Although the length and time-scales of the simulated MAPLE process are very different from the experimental ones (laser pulse duration of 25 ns, penetration depth of ~4.0 μm, and laser fluences from 45 to 750 mJ/cm^2), the same physical regime of thermal confinement [8] is realised in both simulations and experiments. In this irradiation regime, the heat conduction does not contribute to the energy redistribution during the laser pulse and the thermal energy is largely confined within the absorbing region. At the same time, the heating is slow enough to allow the mechanical relaxation of the absorbing region and to avoid the build up of any significant thermoelastic compressive stresses during the laser pulse. The fact that in the simulations and experiments the MAPLE ejection takes place under similar physical conditions suggests that the ejection mechanisms revealed in the simulations are also at work in experiments, albeit at much larger time and length scales.

The absorption by polymer molecules is neglected in the simulations and the effective penetration depth is increased with increasing concentration of polymer molecular in the MAPLE target. Computational cell with dimensions of 40 nm × 40 nm × 60 nm (~650,000 molecules) is used in the simulations with the polymer chains distributed randomly and uniformly in a sample. Each chain contains 100 monomer units with each unit being of the same molecular weight as a

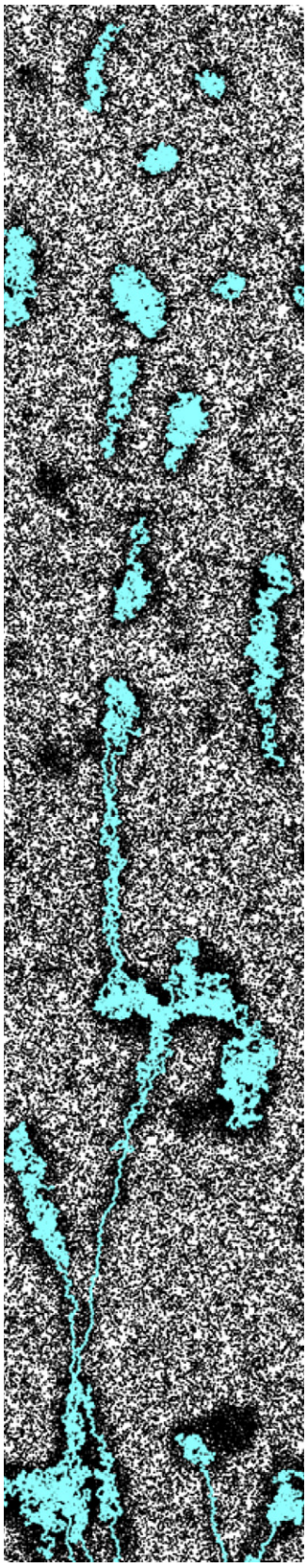

Fig. 3. Snapshot from a MD simulation of MAPLE with a target containing 6 wt.% of polymer. Laser fluence is 9 mJ/cm^2, ~60% above the ablation threshold. Matrix molecules and units of polymer chains are shown by black and blue dots, respectively. The polymer chains are superimposed on top of the image of matrix molecules shown in the background.

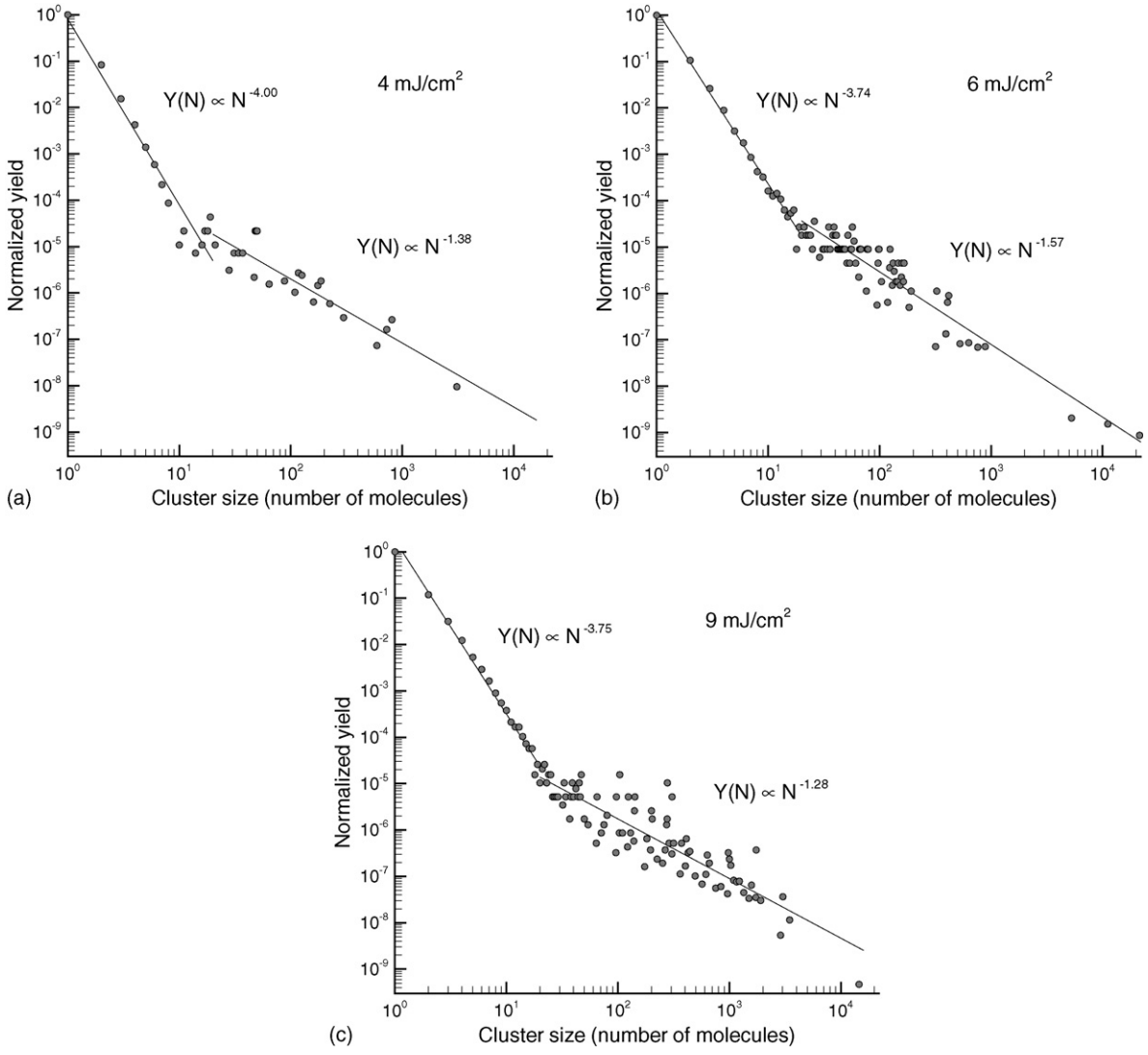

Fig. 4. Cluster size distributions in the ablation plume at 1 ns after irradiation of a MAPLE target with a 50 ps laser pulse at fluences of (a) 4 mJ/cm^2, (b) 6 mJ/cm^2 and (c) 9 mJ/cm^2. The ablation threshold fluence is ~3.5 mJ/cm^2. The initial polymer concentration in the MAPLE target is 6 wt. %. The yield is normalized to the number of individual matrix molecules in the plume. Bimodal power-law distributions are observed over the full range of cluster sizes, where N is the number of matrix molecules and polymer units (mers) in a cluster.

single matrix molecule, 100 Da. This weight corresponds to the weight of a PMMA monomer and is close to the weight of a toluene molecule, 92 Da.

For fluences above the ablation threshold (~3.5 mJ/cm^2), we observe an explosive ejection of an ablation plume consisting of a mixture of gas molecules, clusters and large droplets. Fig. 3 shows a snapshot of a part of the ablation plume taken at 600 ps after the beginning of a MAPLE simulation performed at a laser fluence of 9 mJ/cm^2. General characteristics of the ablation plume, illustrated in this snapshot, are typical for all simulations performed above the ablation threshold. The polymer chains are always ejected as parts of matrix-polymer clusters. Smaller clusters tend to be ejected early in the ablation process and tend to be located in the top part of the plume. Larger clusters are generated later and are ejected with slower velocities. The data obtained from the simulations allows us to perform a quantitative analysis of the composition of the ablation plume and to determine the size distribution of the ejected clusters.

The size distributions of the ejected clusters are shown in Fig. 4 for fluences of 4, 6 and 9 mJ/cm^2. The yield is normalized to the number of individual matrix molecules and is calculated at 1 ns after irradiation. For all fluences we observe cluster size distributions that can be relatively well described by a power-law $Y(N) \propto N^{-t}$ with exponents different for low- and high-mass clusters (N is the size of a cluster that can be defined as the total mass or the number of matrix molecules and polymer units/mers in the cluster). A steep size dependence observed for small clusters (up to 20 molecules) corresponds to the power-law exponents in the range from −3.74 to −4.0. The decay is much slower in the high-mass region of the distributions that can be described by a power law with two to three times larger exponent, from −1.28 to −1.57. Similar bimodal power-law cluster size distributions have been observed earlier in MD

simulations of laser ablation of one-component molecular targets [10]. A weak dependence of the cluster size distributions on fluence and target composition suggests that the bimodal power-law cluster size distribution may be a general characteristic of the ablation plume generated as a result of an explosive decomposition of a target region overheated above the limit of its thermodynamic stability.

The results of the simulations can be related to the experimental mass distributions of surface features shown in Fig. 2. The experimental power-law exponent of −1.65 is close to the ones predicted in the simulations for the high-mass parts of the cluster size distributions. The polymer molecules are ejected with the large matrix clusters that are contributing to the high-mass parts of the distributions. The polymer concentration in large clusters has a weak cluster size dependence and the mass of the polymer material deposited with matrix-polymer clusters can be expected to have a similar distribution. Although much larger molecular clusters, comparable to the laser penetration depth, can be expected to be generated in MAPLE experiments (laser penetration depth is ∼4.0 μm in experiments and ∼50 nm in simulations), a good agreement between the cluster size distributions observed in the simulations and experiments suggests that the mechanisms of molecular ejection revealed in the simulations are likely to be responsible for the cluster ejection under experimental conditions. In particular, based on the simulation results, we suggest that the ejection of large matrix-polymer clusters, followed by evaporation of the volatile matrix in-flight and after the deposition to the substrate, is responsible for the formation of the surface polymer features observed in SEM images of MAPLE deposited films.

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