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Ejection of matrix-polymer clusters in matrix-assisted laser evaporation: Experimental observations

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Abstract. The morphology of polymer films deposited with the matrix-assisted pulsed laser evaporation (MAPLE) technique is explored for various target compositions and laser fluences. Composite targets of 1 to 5 wt.% poly(methyl methacrylate), PMMA, dissolved in a volatile matrix material, toluene, were ablated using an excimer laser at fluences ranging from 0.045 J/cm^2 to 0.75 J/cm^2. Films were deposited on Si substrates at room temperature in a dynamic 100 mTorr Ar atmosphere. Scanning electron microscopy (SEM) imaging revealed that the morphology of the deposited films varied significantly with both laser fluence and PMMA concentration. The morphologies of large deposited particles were similar to that of deflated "balloons". It is speculated that during ablation of the frozen target, clusters comprised of both polymer and solvent ranging from 100 nm to 10 μm in size are ejected and deposited onto the substrate. The solvent begins to evaporate from the clusters during flight from the target, but does not completely evaporate until deposited on the room temperature substrate. The dynamics of the toluene evaporation may lead to the formation of the deflated structures. This explanation is supported by the observation of stable polymer-matrix droplets ejected in molecular dynamics simulations of MAPLE.

1. Introduction

Matrix assisted pulsed laser evaporation (MAPLE) was developed in the late 1990's for the growth of chemoselective polymers [1], polymer thin films [2-4], and polymer nanocomposites [5,6]. The development of nanocomposite thin films is currently a popular venture within both scientific and industrial communities. Recently, a great deal of research has been focused on the formation of carbon nanotube (CNT)-reinforced polymer nanocomposite thin films. Significant increases in mechanical moduli, conductivity, and light emission are just a few examples of the enhanced properties adopted by CNT-doped polymers presented in literature [7-9]. Controlling the dispersion of CNTs, however, is often problematic due to the tendency of CNTs to agglomerate. Laser-assisted co-deposition of polymer matrix and CNTs could provide an attractive alternative to the conventional methods for fabrication of nanocomposite films and coatings.

The work presented in this paper investigates the effect of laser fluence and target polymer-loading on the formation of polymer thin films deposited via MAPLE as a first step in the exploration of MAPLE for the deposition of uniform nanocomposite films. Molecular dynamics simulations and experiments performed in parallel suggest that large clusters of material are being ejected and transported to the substrate, resulting in varied surface features with balloon-like characteristics.

2. Experiment

Targets of poly(methyl methacrylate) (PMMA, M_w = 15,000) dissolved in toluene were prepared with polymer concentrations of 1, 3, and 5 wt.%. Toluene was selected as the matrix solvent due to both its high absorption in the UV and its dissolution characteristics. Targets of each solution were prepared by ultrasonication followed by flash freezing in liquid nitrogen for 300 seconds (T_{melt} toluene ~ 178 K). Depositions were performed onto p-type, single crystal Si substrates at a distance of 7 cm from the target. Prior to deposition, the chamber was pumped down to a base pressure of $3x10^{-5}$ Torr. By dynamically throttling the vacuum systems during deposition, the pressure was stabilized at 100 mTorr while maintaining a continuous Ar flow. The laser fluence was varied from 0.045 J/cm^2 to 0.75 J/cm^2 using an excimer laser (λ= 248 nm, 25 ns FWHM) operating at a frequency of 5 Hz. To avoid target surface effects, such as melting, dynamic rastering of the beam was performed. The deposited films were characterized using a JEOL 6700 scanning electron microscope (SEM).

3. Results and Discussion

The morphology of the deposited PMMA films was found to have a strong dependence on laser fluence and polymer concentration in the target. The number and size of surface features tended to increase with increasing PMMA concentration. Figures 1a-c are representative SEM micrographs showing the morphology dependence on PMMA concentration at a laser fluence of approximately 0.45 J/cm^2. The mean size and density of the surface features increases as a function of concentration from (a) 1 wt.% to (c) 5 wt.%. Figure 1d is an SEM micrograph showing a close up of one of the larger features present in Figure 1c. The feature's deflated balloon like structure is characteristic of this system. Previous results in other systems using chloroform as the matrix solvent also showed similar characteristics [4]. In an ideal case, the toluene molecules ablated from the target are immediately pumped out of the chamber. In this system it is speculated that dynamic porous clusters comprised of both toluene and polymer are ejected from the target and subsequently deposited onto the substrate.

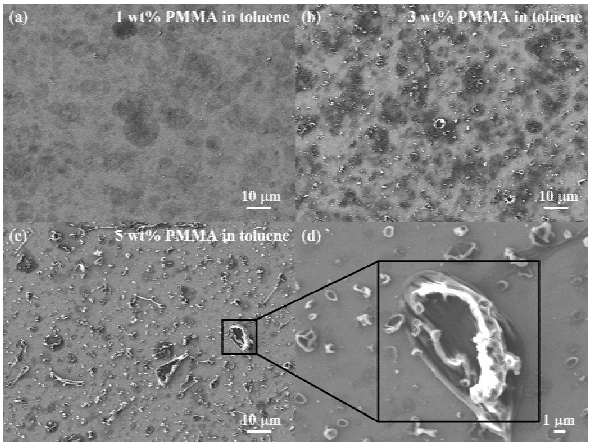

Figure 1. SEM micrographs of PMMA films as a function of PMMA concentration in toluene.

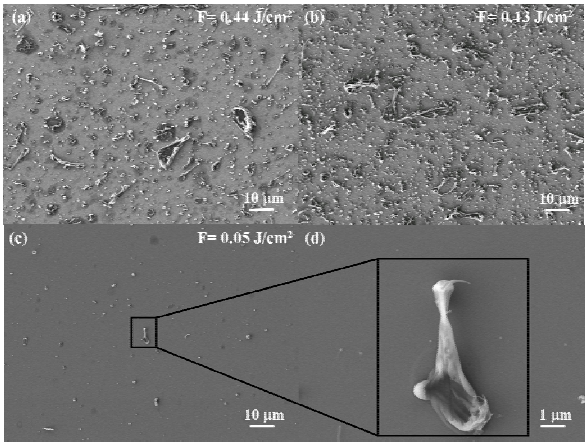

Figure 2. SEM micrographs of PMMA films as a function of laser fluence.

Depositions performed as a function of laser fluence while holding PMMA concentration at 5 wt.% are shown in Figure 2. The density of the surface features increases with laser fluence for fluences below 0.10 J/cm^2; while for fluences exceeding 0.10 J/cm^2 the effect of fluence on the density of surface features is less clear, as a sharp rise in material ejection for fluences approaching 0.10 J/cm^2 was observed. A possible explanation for this result may be that the film in 2c was formed near the threshold for ablation, after which a significant increase in material ejection can be expected within a narrow range of fluences until saturation is achieved [10]. In addition, a sharp threshold for ablation with ejection of a small number of relatively large polymer-matrix droplets was observed in molecular dynamics simulations of the MAPLE process, supporting the association of this fluence with the ablation threshold.

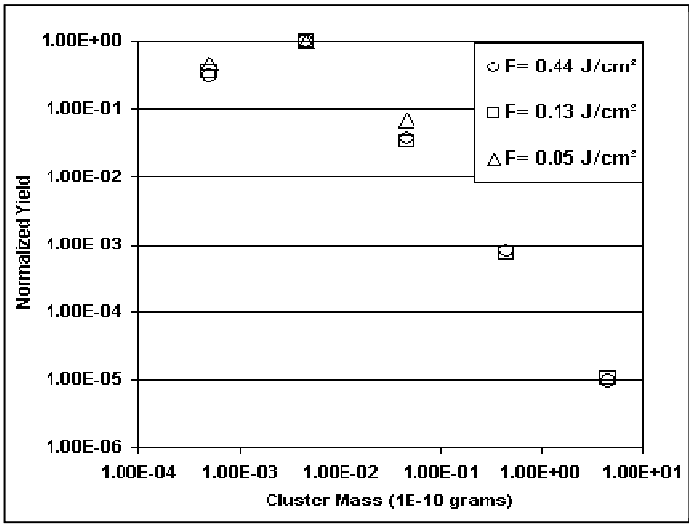

Figure 3. A normalized plot showing particle yield as a function of cluster mass for the three films pictured in Figure 2.

Figure 3 is a plot showing the normalized yield of deposited particles or clusters as a function of mass for the films shown in Figure 2. The plot was generated based on analysis of representative 0.01 mm^2 areas of each film. The masses of the deposited particles were estimated based on measurements of surface areas of each surface feature. The surface areas were converted to volumes and then masses using a conversion factor determined by careful examination of tilted high resolution images of several representative clusters. The conversion factor was determined as a function of the size of the surface feature. The trend is similar for the three fluences in question, suggesting that the mass distribution of the deposited clusters has a weak dependence on laser fluence and, for large clusters, can be described by a power law dependence, $Y(N) \sim N^{-\tau}$, having a power law exponent of ~1.6. A similar power law dependence with an exponent of ~1.3 has been reported for size distributions of high-mass clusters observed in molecular dynamics simulations of laser ablation of molecular targets [11].

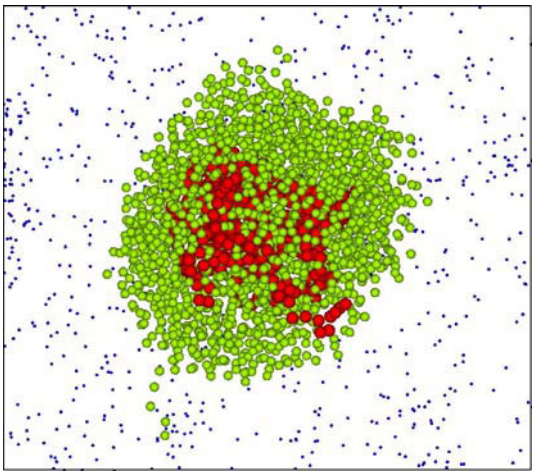

Figure 4. Snapshot from an ablation plume of a cluster ejected in a molecular dynamics simulation of MAPLE performed for a target with 3 wt.% polymer concentration irradiated at a laser fluence of 8 mJ/cm^2.

The role of polymer-matrix clusters in the formation of the observed morphology of the deposited films is supported by the results of molecular dynamics simulations. A snapshot of an ejected polymer-matrix cluster taken from a simulation of MAPLE of PMMA in toluene is shown in Figure 4. The target was comprised of 3 wt.% PMMA in toluene. The green spheres represent toluene molecules, while the red spheres represent PMMA molecules. The small blue spheres represent gas-phase toluene molecules. As the cluster travels through the plume, the polymer concentration increases due to the evaporation of toluene from the outside of the cluster. The cluster is primarily comprised of toluene molecules with only 18 wt.% of PMMA. By the time the snapshot was taken,

the active evaporative cooling of the cluster had slowed down significantly and the cluster most likely retained a substantial amount of matrix at the time of the deposition.

In reflection of the combined experimental – computational results, a scenario for particle formation is proposed. Evaporation of toluene from porous particles leads to the formation of a polymer rich membrane. This membrane effectively decreases the pseudo "diffusion" rate of the remaining toluene molecules. As the toluene continues to evaporate, the membrane temporarily "inflates" until escape passages through the viscous polymer material are formed, thereby inducing a collapse of the polymer membrane and promoting a wrinkled, deflated appearance, such as the one shown in Figure 5.

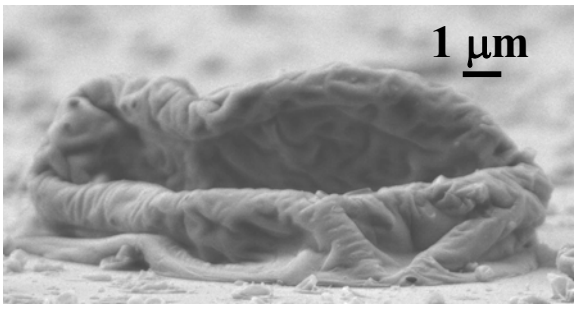

Figure 5. Electron micrograph of a "deflated" balloon type structure of PMMA deposited at a laser fluence of 0.44 J/cm^2.

4. Summary

Thin films of PMMA in toluene were successfully deposited onto Si substrates via MAPLE. Both laser fluence and polymer concentration were varied. Experiments and molecular dynamics simulations were run simultaneously to investigate the laser-solid interactions governing film formation; specifically, as a function of laser fluence and polymer loading. The morphology of the deposited films suggests that cluster ejection and subsequent deposition onto the substrates is occuring. In general, as polymer concentration and fluence were increased, the number density and size of surface features also increased.

Acknowledgments

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