

## Resonant infrared pulsed-laser deposition of polymer films using a free-electron laser

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Thin films of polyethylene glycol (MW 1500) have been prepared by pulsed-laser deposition (PLD) using both a tunable infrared ( $\lambda=2.9 \mu\text{m}$ ,  $3.4 \mu\text{m}$ ) and an ultraviolet laser ( $\lambda=193 \text{ nm}$ ). A comparison of the physicochemical properties of the films by means of Fourier transform infrared spectroscopy, electrospray ionization mass spectrometry, and matrix-assisted laser desorption and ionization shows that when the IR laser is tuned to a resonant absorption in the polymer, the IR PLD thin films are identical to the starting material, whereas the UV PLD show significant structural modification. These results are important for several biomedical applications of organic and polymeric thin films. © 2001 American Vacuum Society. [DOI: 10.1116/1.1387052]

### I. INTRODUCTION

Polyethylene glycol (PEG) is a technologically important polymer with many biomedical applications.<sup>1</sup> Examples include tissue engineering,<sup>2</sup> spatial patterning of cells,<sup>3,4</sup> drug delivery coatings,<sup>5,6</sup> and antifouling coatings.<sup>7</sup> In these applications, a need exists for a technique capable of depositing thin, uniform, and adherent coatings of PEG. Whereas in some cases it is acceptable to deposit chemically modified PEG polymeric material,<sup>7,8</sup> in drug delivery and *in vivo* applications it is important that there is no difference in the chemical and structural properties of PEG films compared with the bulk polymer.

In this article, we report the first successful pulsed-laser deposition (PLD) of thin polyethylene glycol (PEG) films using a tunable IR source in the midinfrared. A direct comparison is made between PEG films grown with an UV laser (193 nm) and a tunable infrared laser. The IR laser is tuned to be resonant with the O–H ( $2.9 \mu\text{m}$ ) or C–H ( $3.4 \mu\text{m}$ ) stretch mode in PEG. The films were characterized by means of Fourier transform infrared spectroscopy (FTIR), electrospray ionization mass spectrometry (ESI), and matrix-assisted laser desorption and ionization time-of-flight mass spectrometry (MALDI). The comparisons show that when the IR laser is tuned to a resonant feature in the organic material, the IR PLD films retain the optical, structural, and

physical characteristics of the bulk PEG material, whereas the UV PLD deposited PEG materials do not. In addition, the results also show clearly that the mechanism of IR PLD is fundamentally different than UV PLD. These results are very important in the context of such biomedical technologies as drug-delivery coatings and *in vivo* applications where it is crucial to effect transfer of polymeric coatings without significant chemical or physical modification to the polymer.

### II. BACKGROUND

Pulsed-laser deposition has been an extremely successful technique for depositing thin films of a large variety of inorganic materials.<sup>9</sup> PLD has also been applied to the growth of thin polymeric and organic films, albeit with varying degrees of success. For example, when PLD is used to fabricate chemical sensors from polymer–carbon nanocomposites, both the molecular weight distribution and the chemical structure of the polymeric material are substantially altered, but the required functional groups for the sensor remain intact.<sup>10</sup> In other cases, the damage caused during UV ablation is limited to a reduction in the molecular weight with the chemical structure remaining intact.<sup>11</sup> It has been shown that certain polymers such as poly-methyl methacrylate (PMMA), poly-tetrafluoroethylene (PTFE), and poly- $\alpha$ -methyl styrene (PAMS), undergo rapid depolymerization during UV laser ablation, with the monomer of each strongly present in the ablation plume.<sup>12–14</sup> For these polymers, the molecular weight distribution of the deposited thin-film ma-

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terial can be increased by simply raising the substrate temperature.<sup>15</sup> Therefore, even in the most successful cases of UV PLD of polymers there is an intense interaction between the target material and laser resulting in chemical modification of the polymer during ablation. If repolymerization is incomplete at the substrate, this can lead to both a reduction of molecular weight and a change in chemical structure.

The mechanism for UV ablation of organic materials has been debated for some time. In the photochemical model of ablation,<sup>16,17</sup> absorption of an UV photon leads to direct bond dissociation and fragmentation of the organic molecule. In the photothermal model,<sup>18,19</sup> the energy absorbed by the UV photon is rapidly converted to heat and the polymer undergoes pyrolysis. Rapid pyrolysis results in depolymerization of target material in the plume; repolymerization occurs on the substrate, possibly initiated by the pressure of free radicals.<sup>12–15,19</sup>

Ablation may also proceed through the absorption by extrinsic<sup>20</sup> or laser-generated impurities such as color centers.<sup>21</sup> Extrinsic impurities may absorb the light directly resulting in local heating by electron–phonon coupling, or the interaction length may be increased through scattering, resulting in absorption by the polymer. Thin films or polystyrene doped with anthracene,<sup>22</sup> and polyethylene oxide with a ZrO additive<sup>23</sup> have been successfully ablated in this way.

In general, the interaction between organic molecules and UV light is very complicated, occurring as it does with extreme rapidity<sup>24</sup> and through many different excitation–relaxation pathways.<sup>25</sup> This certainty seems to present a number of challenges to polymer film growth using UV lasers.

### III. MOTIVATION (FOR THIS EXPERIMENT)

For organics, an alternative approach to PLD with UV lasers is matrix-assisted pulsed-laser evaporation (MAPLE), in which roughly 0.1% to 1% of a material to be deposited is dissolved in an appropriate solvent and frozen to form an ablation target.<sup>26–28</sup> The UV laser light interacts mostly with the solvent and the guest material is thus ablated much more gently than in conventional PLD. While this can result in smooth uniform films suitable for a variety of applications, it nevertheless requires that the polymer of interest be soluble in a noninteracting solvent. The one serious disadvantage to MAPLE is that the deposition rate is about an order of magnitude lower than in conventional PLD.<sup>26,27</sup>

In the early days of PLD, IR lasers were extensively used for deposition,<sup>29,30</sup> although UV lasers have now become the workhorse of PLD research in inorganic materials. The complexity of the UV-induced photoablation and photodecomposition channels leads one to wonder whether IR PLD might be an appropriate alternative for deposition of organic materials. This is particularly true given the availability of broadly tunable, high-average-power sources such as the free-electron laser in the midinfrared. Recently, for example,

such an approach has been successfully applied to the matrix-assisted laser desorption and ionization mass spectroscopic technique.<sup>31</sup>

### IV. EXPERIMENT

The light source of the IR PLD films was the W. M. Keck Foundation Free-Electron Laser (FEL) at Vanderbilt University. The Vanderbilt FEL produces a 4  $\mu\text{s}$  macropulse at a repetition rate of 30 Hz; the macropulse in turn comprises some 11 400 1 ps micropulses separated by 350 ps. The energy in each micropulse is of order 10  $\mu\text{J}$ , so that the peak unfocused power in each micropulse is very high ( $\sim 10^7$  W). The average power of the FEL is of order 2–3 W and it is continuously tunable over the range 2–10  $\mu\text{m}$ .

The characteristics of the laser are discussed in greater detail elsewhere.<sup>31,32</sup> For the IR PLD films the macropulse fluence was between 2 and 9  $\text{J}/\text{cm}^2$ , the target substrate distance was 3 cm, and the spot size was 0.0022  $\text{cm}^2$ . The background pressure in the chamber during deposition was between  $10^{-5}$  and  $10^{-6}$  Torr. A typical deposition rate for these conditions ( $\lambda=3.4$   $\mu\text{m}$ , fluence = 6.8  $\text{J}/\text{cm}^2$ , spot size = 0.0022  $\text{cm}^2$ ) was 140  $\text{ng}/\text{cm}^2$  macropulse. Amorphous PEG is a soft material, thus making contact profilometry problematic. For a film deposited using 10 000 macropulses, this corresponds to a film thickness of approximately 10  $\mu\text{m}$  using the bulk density of amorphous PEG (Ref. 33) and the areal density measured after deposition.

Films were also deposited using nonresonant radiation from the FEL. The laser was tuned to 3.3  $\mu\text{m}$  ( $3030$   $\text{cm}^{-1}$ ), at which PEG is nonabsorbing. The fluence was 6.1  $\text{J}/\text{cm}^2$  and all other experimental parameters were the same as in the resonant (3.4  $\mu\text{m}$ , 2.9  $\mu\text{m}$ ) cases. The deposition rate was 68  $\text{ng}/\text{cm}^2$  macropulse. We observe that there are significant differences in the infrared absorbance spectrum, yet the ESI mass spectrum is nearly identical to the resonant IR case. It is possible that the material is modified in such a way as to be difficult, if not impossible, to detect by ESI or MALDI. It is also possible that the ablation proceeds due to a multiple photon process, which is certainly possible at the high fluences at which the FEL operates. Further study is needed in order to clarify these points and the results will be discussed elsewhere.

For purposes of comparison, an ArF excimer laser (Lambda Physik 305;  $\lambda=193$  nm; FWHM=30 ns) was used for UV PLD. The experimental setup has been described in detail previously.<sup>26</sup> The laser was operated at a repetition rate of 10 Hz with the fluence varied between 150 and 300  $\text{mJ}/\text{cm}^2$ . The target substrate distance was 3 cm. The spot size was between 0.06 and 0.13  $\text{cm}^2$  and the beam was rastered over the entire surface of the 1-in.-diam rotating target (35 rpm). Our starting material is PEG 1450 Carbowax (Altech Associates, Deerfield, IL). Material was collected on NaCl plates and glass microscope slides held at room temperature for postdeposition analyses. The background pressure in the chamber during deposition was between  $10^{-5}$  and  $10^{-6}$  Torr. A typical deposition rate for these conditions (fluence = 200  $\text{mJ}/\text{cm}^2$ , spot size = 0.13  $\text{cm}^2$ ) was 10

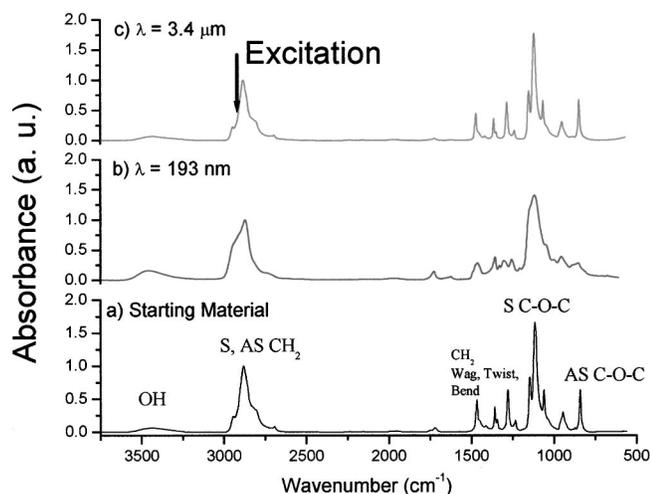


FIG. 1. Infrared spectrum of (a) starting material, (b) UV PLD ( $\lambda=193$  nm), and (c) IR PLD film ( $\lambda=3.4$   $\mu\text{m}$ —resonant with CH stretch). In (a), important modes are labeled (S=symmetric, AS=antisymmetric). The arrow in (c) indicates the laser wavelength used for excitation in the deposition of the IR PLD film.

ng/cm<sup>2</sup> pulse. A film deposited using 10 000 shots will be approximately 0.8  $\mu\text{m}$  thick using the approach outlined above for the resonant IR case.

Polyethylene glycol samples were analyzed using FTIR, ESI,<sup>34</sup> and MALDI.<sup>35</sup> Infrared spectra were recorded for the films using either a Bruker IFS 66 or Nicolet Magna-IR 750 Fourier transform infrared spectrometer. PEG samples were extracted from the surface with 1 ml of methanol, and then evaporated to dryness in a vial. The samples were redissolved in 25  $\mu\text{L}$  of methanol. For ESI, 20  $\mu\text{L}$  aliquots of the solution were mixed with an equal volume of KCl in water, to produce a final KCl concentration of 1 mM. Samples were electrosprayed and analyzed on a Thermoquest LCQ ion trap mass spectrometer. For MALDI, 2  $\mu\text{L}$  of the reconstituted sample was mixed with saturated matrix solution [2-(4-hydroxyphenylazo)benzoic acid, HABA, or dithranol/silver trifluoroacetate] and evaporated on the probe tip. Samples were desorbed with a 337 nm laser and spectra were obtained on a time-of-flight mass spectrometer.

## V. DISCUSSION AND RESULTS

The midinfrared absorbance spectra of a drop cast, UV PLD, and IR PLD film are shown in Fig. 1. For the sake of comparison, the absorbance spectra have been normalized to the CH<sub>2</sub> symmetric stretching feature at 2880  $\text{cm}^{-1}$ . The spectra of the films deposited using IR light are identical, so only one ( $\lambda=3.4$   $\mu\text{m}$ ) is shown for the sake of clarity. At 3.4  $\mu\text{m}$ , the IR laser is resonant with the C–H stretch in PEG. The spectra of the starting material and the IR PLD films' spectra exhibit no discernible differences. The spectrum of the film deposited using UV light, however, has changed dramatically. The OH absorbance has increased by a factor of 2.5 relative to the starting material and IR PLD film, while the maximum is shifted to a higher wave number ( $\Delta\omega=20$   $\text{cm}^{-1}$ ). The C–O–C symmetric stretching band at 1110  $\text{cm}^{-1}$

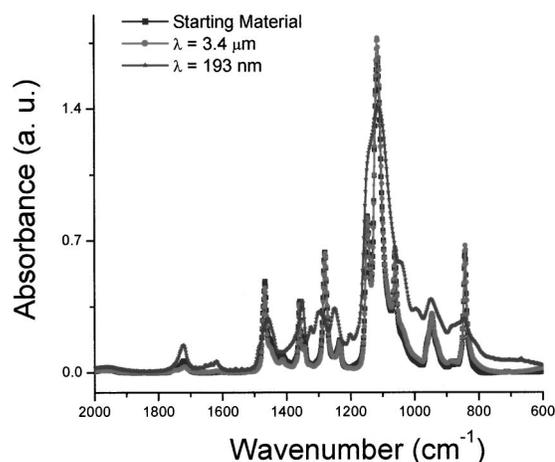


FIG. 2. Expanded view of fingerprint region of infrared spectra. Note the agreement between the IR PLD and drop cast films' spectra. The UV PLD film's spectra show strong evidence for chemical modification.

is reduced in intensity and the absorbance maximum of the symmetric CH<sub>2</sub> stretch is shifted ( $\Delta\omega=-15$   $\text{cm}^{-1}$ ) to 2867  $\text{cm}^{-1}$ . Figure 2 shows an expanded view of the fingerprint region in which the CH<sub>2</sub> wag, twist, and bend modes are modified significantly in the UV PLD experiment. We have used Refs. 23 and 36 as aids in spectral assignment.

One possible explanation of the shifts observed in the UV PLD films' spectrum involves scission of a C–O bond in the middle of the polymer. One fragmented chain could abstract a proton from the other fragmented chain, resulting in a terminal double bond on one of the fragments and an additional OH group on the other. There is an additional small band at 1650  $\text{cm}^{-1}$  that is consistent with the appearance of a terminal alkene. Fully understanding the exact nature of the

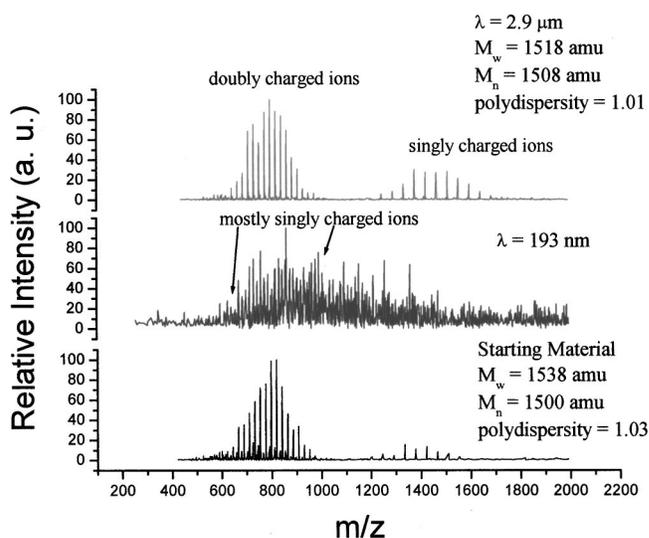


FIG. 3. Electrospray ionization mass spectrum of (a) starting material, (b) UV PLD ( $\lambda=193$  nm), and (c) IR PLD film ( $\lambda=2.9$   $\mu\text{m}$ —resonant with OH stretch). The UV PLD film's spectra are not recognizable when compared with the starting material. The calculated molecular weights of the IR PLD film and the starting material are in very close agreement.

chemical modification of the UV PLD films, however, will require further study.

Both ESI and MALDI have been used to determine the molecular weight distributions in the IR and UV PLD films. In Fig. 3, the ESI results are shown. The UV PLD film shows almost no recognizable pattern relative to the standard in the mass spectrum. In contrast, the IR PLD film has a very similar mass spectrum to the starting material. When the laser is tuned to 2.9  $\mu\text{m}$ , it is resonant with the OH stretch in PEG. By calculation based on the position of the peaks, we see that the mass average ( $M_w$ ) for starting material (1538) and IR PLD (2.9  $\mu\text{m}$ =1518; 3.4  $\mu\text{m}$ =1528) are identical to well within one monomer unit (44 amu). Additionally, the number average ( $M_n$ ) for starting material (1500 amu) and IR PLD (2.9  $\mu\text{m}$ =1508 amu; 3.4  $\mu\text{m}$ =1507 amu) are similarly close. The polydispersity ( $M_w/M_n$ ) for the IR PLD films (1.01–1.05) is nearly the same as the starting material (1.03).

We note that there are some differences between the ESI spectrum of the IR PLD and standard samples in the ratios of singly and doubly charged envelopes of ions. These differences can be attributed to variations in the ratio of added KCl to polymer in the ESI samples. As this ratio increases, more multiply charged ions are observed. Since the amount of polymer extracted from the surfaces varies from sample to sample, it is difficult to standardize this ratio. However,  $M_n$  and  $M_w$  values are calculated based on the contributions from singly, doubly, and triply charged ions, and thus account for shifts in the charge state distribution. ESI spectra obtained with various ratios of Cl to PEG standards have shown that  $M_n$  and  $M_w$  will vary somewhat with this ratio; consequently, while small variations in molecular weight from sample to sample are not significant, large changes would be apparent.

MALDI measurements have also been performed on all three films. These results agree with the ESI mass spectra. They also verify that the region between  $m/z=600$  and  $m/z=1200$  of the UV PLD sample is largely comprised of singly charged ions, thus suggesting that we may bracket the mass average of the UV PLD film between 900 and 1000 amu.

It was also necessary to obtain the MALDI spectrum of the UV PLD sample under completely different conditions (using dithranol/silver trifluoroacetate) in order to observe signals. The ions observed are different in chemical composition than those formed from the PEG standard. This is consistent with the observation that most of the ions observed in the ESI spectrum of the PLD sample cannot be related to the starting material in a simple way. Similar to the FTIR spectra, the mass spectra show that IR PLD films and the starting material are nearly identical whereas the UV PLD films is shifted lower in molecular weight and chemically altered.

The mass and FTIR spectra indicate that in IR PLD the polymer chains are transferred intact with the same physicochemical properties as the starting material. This is in stark contrast to UV PLD in which the initial electronic excitation is either converted to heat which results in depolymerization and subsequent repolymerization<sup>12–15,18,19,21</sup> on the substrate,

or results in bond rupture and the deposition of modified oligomeric fragments.<sup>16,17</sup> The fact that individual FEL micropulses are separated by 350 ps indicates that the anharmonic vibrational modes excited by the laser are probably fully relaxed between micropulses;<sup>37</sup> however, since thermal diffusion times are comparable to the duration of the macropulse, it is also likely that the temperature of the ablation target is gradually rising throughout the macropulse. This complicates the analysis of the ablation mechanism. Rapid relaxation of anharmonic vibrational modes could mean that the ablation is a single-photon process; on the other hand, heating of the target material during the macropulse could produce efficient ablation by “preheating” or more effective heating by strong coupling between local and dispersed phonon modes. Experiments are underway using different FEL pulse structures in order to investigate these questions. If it is, in fact, the case that the ablation is primarily initiated by a single-photon excitation, then polymer chains must surely be transferred intact because the photon energy involved (0.36–0.42 eV) is far below the energy required for electronic excitation and direct bond rupture.

## VI. CONCLUSION

Analysis of thin films of PEG deposited by laser ablation using an infrared tunable source shows that the IR source is tuned to a resonant absorption in the polymer, the polymer is transferred to the growth surface without chemical or structural modification. In contrast, the use of an UV laser for deposition results in severe photochemical modification of the polymer material appearing in the films. Such physical and chemical rearrangement of the polymer renders UV PLD unsuitable for applications such as drug delivery coatings and *in vivo* applications in which the polymer coating is required to be unchanged from the bulk material. Moreover, the use of a resonantly tunable infrared source provides a potentially more general approach to polymer thin-film deposition than either UV PLD, where undesirable photochemical or photothermal effects can occur, or MAPLE, which requires a noninteractive, light-absorbing matrix for film deposition. In addition, tunable infrared laser sources such as free-electron lasers with their high macropulse energies and high average powers may well provide new opportunities for studying the mechanisms of polymer ablation and mode-specific chemistry in such processes as IR PLD.

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