Appl. Phys. A 73, 121–123 (2001) / Digital Object Identifier (DOI) 10.1007/s003390100884

Applied Physics A
Materials
Science & Processing

Rapid communication

Vapor deposition of intact polyethylene glycol thin films

D.M. Bubb[1,*], **B.R. Ringeisen**[1], **J.H. Callahan**[2], **M. Galicia**[3], **A. Vertes**[3], **J.S. Horwitz**[1], **R.A. McGill**[1], **E.J. Houser**[1], **P.K. Wu**[1,**], **A. Piqué**[1], **D.B. Chrisey**[1]

[1] Naval Research Laboratory, Surface Modification Branch, Code 6370, 4555 Overlook Ave., SW, Washington, D.C. 20375, USA
[2] Naval Research Laboratory, Chemical Dynamics and Diagnostics Branch, Code 6115, 4555 Overlook Ave., SW, Washington, D.C. 20375, USA
[3] Department of Chemistry, George Washington University, Washington, D.C. 20001, USA

Received: 2 March 2001/Accepted: 5 March 2001/Published online: 23 May 2001 – © Springer-Verlag 2001

Abstract. Thin films of polyethylene glycol (PEG) of average molecular weight, 1400 amu, were deposited by both matrix-assisted pulsed laser evaporation (MAPLE) and pulsed laser deposition (PLD). The deposition was carried out in vacuum ($\sim 10^{-6}$ Torr) with an ArF ($\lambda = 193$ nm) laser at a fluence between 150 and 300 mJ/cm^2. Films were deposited on NaCl plates, Si(111) wafers, and glass slides. The physiochemical properties of the films are compared via Fourier transform infrared spectroscopy (FTIR), electrospray ionization (ESI) mass spectrometry, and matrix-assisted laser desorption and ionization (MALDI) time-of-flight mass spectrometry. The results show that the MAPLE films nearly identically resemble the starting material, whereas the PLD films do not. These results are discussed within the context of biomedical applications such as drug delivery coatings and in vivo applications where there is a need for transfer of polymeric coatings of PEG without significant chemical modification.

PACS: 61.41.+e; 81.05.Lg; 81.15.Fg

Polyethylene glycol (PEG) is a technologically important polymer with many biomedical applications [1]. Examples include tissue engineering [2], spatial patterning of cells [3, 4], drug delivery coatings [5, 6], and anti-fouling coatings [7]. 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 [7, 8], in biomedial applications it is important that there is no difference in the chemical and structural properties of PEG films compared to the bulk polymer. Recently, a new technique for depositing polymeric and organic thin films known as matrix-assisted pulsed laser evaporation (MAPLE) has been developed [9]. This method is to be distinguished from conventional pulsed laser deposition (PLD) in that the target preparation methods and laser-material interactions are significantly different. In MAPLE, the material to be deposited is dissolved in an appropriate solvent, typically 0.1 to 2.0 wt. % concentrated, and frozen solid. The composite target is evaporated using a pulsed laser. The vaporized solvent does not form a film and is pumped away by the vacuum system. In PLD, a solid target is used with laser beam interacting directly with the material to be deposited. In some cases, strong absorption of UV light can lead to severe photochemical damage of the organic material. During MAPLE, the laser beam is absorbed primarily by the solvent, which minimizes damage to the guest material.

PLD at 1–2 J/cm^2 has long been used to deposit thin films of a variety of inorganic materials including superconductors, ferroelectrics, metals, and transparent conducting oxides [10]. When depositing these materials, the ablation plume consists predominantly of neutral atoms, small molecules and ions. The constituent elements arrive at the substrate in the appropriate ratios and form a film with correct stoichiometry and phase. By adjusting the deposition conditions on a lattice-matched substrate, one can grow oriented, crystalline and even epitaxial films. When ablating polymeric material, the mechanism of transfer is necessarily very different. Generally speaking, studies involving ablation of polymers have concentrated on two classes of materials, addition and condensation polymers. Studies on addition polymers [11] have shown that there are some polymers for which monomers is strongly present in the ablation plume, and the average molecular weight of deposited material can be varied independently of the target material by properly adjusting the temperature of the substrate. A thermal mechanism has been proposed [12, 13] in which the ablated material is rapidly (nearly instantaneously) heated above the onset of pyrolytic decomposition, resulting in a chain depolymerization reaction. When the vapor arrives on the heated substrate, it repolymerizes. While the resulting films are very good for addition polymers, such as poly-tetra flouroethylene (PTFE) and polymethyl methacrylate (PMMA), it is doubtful whether one can deposit films of condensation polymers with intact structure in this fashion [14]. Accordingly, it appears that one can only

---

[*] Corresponding author.
(Fax: +1-202/767-5301, E-mail: dbubb@nrl.navy.mil)

[**] *Permanent address*: Southern Oregon University, Ashland, Oreg. 97520, USA

use PLD as a tool to deposit films that reflect the chemical and physical structure of the target material for a limited class of polymers. In contrast, MAPLE is a technique that can be used to deposit a wide variety of polymeric and organic thin films [9, 15] provided that a suitable solvent may be found.

In this paper we demonstrate chemically and structurally pure thin films of PEG films grown by the vapor deposition technique known as MAPLE [9]. The deposited films are characterized by Fourier transform infrared spectroscopy (FTIR), matrix assisted laser desorption and ionization (MALDI) and electrospray ionization (ESI) mass spectrometry. The molecular weight characterization of deposited films is simplified by the fact that PEG enjoys wide use as a molecular weight standard for techniques such as MALDI [16]. While a polymer thin film can be grown using a PEG target with PLD, analysis of the film structure shows that the films undergo photochemical modification compared with the starting material. Our films grown by PLD are similar to those reported in the literature [17].

1 Experiment

The experimental apparatus has previously been described in detail [9]. For both PLD and MAPLE, PEG (Alltech Associates, Deerfield, Ill.) was used. We verified the average molecular weight of the PEG by gel permeation chromatography (GPC) to be 1400 amu. For MAPLE, deionized water was used as a matrix ($R > 18\,\mathrm{M\Omega}$). It was observed that the deposition rate could be increased by the addition of a small amount of isopropanol alcohol into the mixture (~ 5 wt. %). For MAPLE, a 1″ (2.54 cm) aluminum target holder is filled with PEG dissolved in solvent, then clamped to a small metal plate, inverted, and flash frozen in liquid nitrogen. The frozen target is mounted on a refrigerated assembly which can be cooled to 100 K. Typically, when using water as a matrix, the target was held at ~ 240 K. An ArF excimer laser (Lambda Physik 305; $\lambda = 193$ nm; FWHM $= 30$ ns) was used for both MAPLE and PLD. The laser was operated at a repetition rate of 10 Hz with the fluence varied between 150 and 300 mJ/cm^2. The target substrate distance was 3 cm. The spot size was 0.06 cm^2 and the beam was rastered over the entire surface of the 1″ diameter rotating target (35 rpm). Material was collected on Si(111) wafers, NaCl plates, and glass microscope slides held at room temperature for post-deposition analyses. The background pressure in the chamber during deposition was $\sim 10^{-6}$ torr.

Polyethylene glycol samples were analyzed using ESI [18] and MALDI [19]. PEG samples were extracted from the surface with 1 ml of methanol and then evaporated to dryness in a vial. The samples were re-dissolved in 25 μL of methanol. For ESI, 20 μL aliquots of the solution were mixed with an equal volume of KCl in water, to produce a final KCl concentration of 1000 μM. Samples were electrosprayed and analyzed on a Thermoquest LCQ ion trap mass spectrometer. For MALDI, 2 μL of the reconstituted sample was mixed with saturated matrix solution [2-(4-hydroxyphenylazo)benzoic acid, HABA, or dithranol/silver trifluoroacetate, AgTFA] 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.

2 Results and discussion

The infrared spectra of PLD, MAPLE and drop-cast PEG films are shown in Fig. 1. The PLD and MAPLE films have had a sloping baseline subtracted from their spectra, and the spectral feature at 1115 cm^{-1} has been used for normalization. A Nicolet FTIR spectrometer was used to record the spectra in transmission between 400 and 4000 cm^{-1}. All of the spectra are fairly similar. However, there is a new band in Fig. 1a which does not appear in the other (MAPLE and drop-cast) spectra at around 1650 cm^{-1}. We assign this to a terminal alkene band which arises as the result of scission that occurs during the PLD process. In the inset of Fig. 1, an expanded region of the spectra between 1200 and 1400 cm^{-1} is shown. These bands are associated with the CH$_2$ wag and twist modes and are clearly modified in the PLD film's spectrum. Additionally, the OH band has increased in strength relative to the other bands ($\sim 2.5\times$) and is shifted to slightly higher wavenumber ($\Delta\omega \approx 20\,\mathrm{cm}^{-1}$). In examining the spectrum of the MAPLE deposited film, there is no evidence for chemical modification with respect to the starting material. The major spectral features are present in the same intensity ratios as in the drop-cast film.

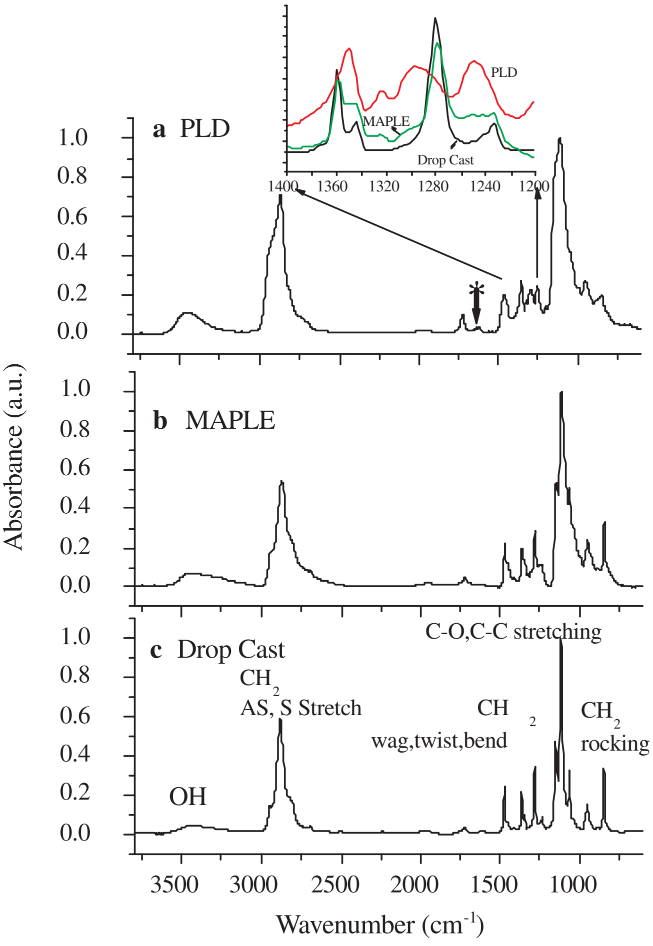

Fig. 1a–c. Infrared spectrum of **a** PLD, **b** MAPLE, and **c** drop-cast (starting material) films. *Inset* shows expanded region between 1200 and 1400 cm^{-1} for all films where the PLD film shows significant differences from the starting material. In **a**, the appearance of an additional band is marked by an *asterisk*

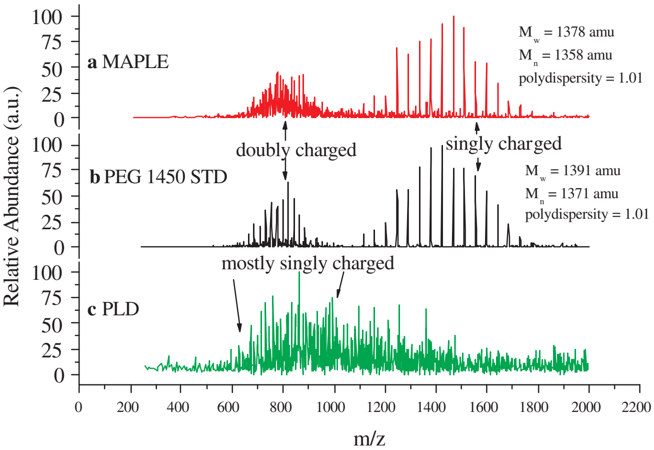

Fig. 2a–c. ESI mass spectrum of **a** MAPLE film, **b** starting material, and **c** PLD film

One possible explanation for the shifts observed in the PLD film's spectrum involves scission in the middle of the polymer chain between a C–O bond. One fragmented chain could abstract a proton from the other fragmented chain. This would result in a terminal double bond on one of the fragments and an additional OH group on the other. Fully understanding the exact nature of the chemical modification of the PLD films, however, will require further study.

To complement the infrared spectral data, we performed molecular weight analyses on the starting material and films grown by PLD and MAPLE. Both ESI and MALDI were used. In Fig. 2, the ESI results are shown. The PLD film shows almost no recognizable pattern relative to the standard in the mass spectrum. In contrast, the MAPLE film has a very similar mass spectrum to the starting material. Examining the singly charged ion envelope in the mass spectrum, we see that the mass average for starting material (1391 amu) and MAPLE (1378 amu) are well within one monomer unit (44 amu). Additionally, the number average for the starting material (1377 amu) and MAPLE (1358 amu) are similarly close. The polydispersity $\left(\frac{M_w}{M_n}\right)$ for the MAPLE film (1.01) is the same as the starting material (1.01). We note that there are some differences between the ESI spectrum of the MAPLE and standard samples, particularly in the doubly charged envelope of ions. The ESI spectrum of the MAPLE sample is characterized by more doubly charged ions, which result from the addition of K^+ and Na^+ ions to the same oligomer (in addition to the case where two K^+ ions are attached). This occurs because the MAPLE sample is extracted from a glass surface, and numerous sodium ions are picked up by the sample in the extraction process. Moreover, the signal-to-noise ratio of the MAPLE spectrum is lower, and lower m/z chemical noise peaks are relatively more abundant in the MAPLE spectrum.

MALDI measurements were also 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 PLD sample is largely comprised of singly charged ions, thus allowing us to bracket the mass average of the PLD film between 900 and 1000 amu. It was also necessary to obtain the MALDI spectrum of the PLD sample under completely different conditions (using dithranol/AgTFA) 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 MAPLE films and the starting material are nearly identical, whereas the PLD film is shifted lower in molecular weight and chemically altered.

The FTIR, ESI, and MALDI-TOF results clearly demonstrate that MAPLE is a laser-based technique capable of depositing PEG thin films that have the same chemical structure as the bulk polymer. In contrast, PLD is a film growth technique suitable for only a small class of polymers and most often results in chemical modification of the polymer material. This renders PLD undesirable for biomedical applications that require coatings with bulk chemical structures. Coupling these results with those obtained for other organic materials [9, 15] shows that MAPLE is a very versatile deposition tool for organic thin films. The development of the MAPLE technique represents a substantial advancement in thin film deposition science.

Acknowledgements. This work has been supported by the Office of Naval Research. DMB would like to thank J.M. Joseph for useful discussion.

References

1. J.M. Harris, J.M. Dust, R.A. McGill, P.A. Harris, M.J. Edgell, R.M. Sedaghat-Herati, L.J. Karr, D.L. Donnelly: In *Water-Soluble Polymers*, ed. by S.W. Shalaby, C.L. McCormick, G.B. Butler (ACS Symposium Series **467**, ACS, Washington, D.C. 1991) p. 418–429
2. L.J. Suggs, E.Y. Kao, L.L. Palombo, R.S. Krishnan, M.S. Widmer, A.G. Mikos: In *Polymers for Tissue Engineering*, ed. by M.S. Shoichet, J.A. Hubbell (VSP, Utrecht 1998) p. 99–112
3. N. Patel, R. Padera, G.H.W. Sanders, S.M. Cannizzaro, M.C. Davies, R. Langer, C.J. Roberts, S.J.B. Tendler, P.M. Williams, K.M. Shakesheff: FASEB J. **12**, 1447 (1998)
4. S.O. Vansteenkiste, S.I. Corneille, E.H. Schact, X. Chen, M.C. Davies, M. Moens, L.V. Vaeck: Langmuir **16**, 3330 (2000)
5. Y. Kaneko, K. Sakai, T. Okano: In *Biorelated Polymers and Gels*, ed. by T. Okano (Academic Press, New York 1998) p. 29–69; M. Yokoyama: In *Biorelated Polymers and Gels*, ed. by T. Okano (Academic, New York 1998) p. 193–229
6. C.M. Henry: Chem. Eng. News **78**, 49 (2000)
7. M.N. Mar, B.D. Ratner, S.S. Yee: Sensors Actuators B **54**, 125 (1999)
8. P. Favia, R. d'Agostino: Surf. Coatings Technol. **98**, 1102 (1998)
9. A. Piqué, R.A. McGill, D.B. Chrisey, D. Leonhardt, T.E. Mslna, B.J. Spargo, J.H. Callahan, R.W. Vachet, R. Chung, M.A. Bucaro: Thin Solid Films **355-356**, 536 (1999)
10. D.B. Chrisey, G.K. Hubler (Eds.): *Pulsed Laser Deposition of Thin Solid Films* (Wiley, New York 1994)
11. G.B. Blanchet: J. Appl. Phys. **80**, 4082 (1996) and references therein
12. G.B. Blanchet, C.R. Fincher Jr., C.L. Jackson, S.I. Shah, K.H. Gardner: Science **262,** 719 (1993)
13. G.B. Blanchet, C.R. Fincher Jr: Appl. Phys. Lett. **65**, 1311 (1994)
14. S.G. Hansen: J. Appl. Phys. **68** 1878 (1990)
15. B.R. Ringeisen, J. Callahan, P. Wu, A. Piqué, B. Spargo, R.A. McGill, M. Bucaro, H. Kim, D.M. Bubb, D.B. Chrisey: Langmuir (in press)
16. X. Fei, K. Murray: Anal. Chem. **68**, 3555 (1996)
17. P. Manoravi, M. Joseph, N. Sivamakur: J. Phys. Chem. Solids **59**, 1271 (1999)
18. T. Nohmi, J.B. Fenn: J. Am. Chem. Soc. **114**, 3241 (1992)
19. G. Montaudo, M.S. Montaudo, C. Puglisi, F. Samperi: Rapid Comm. Mass Spectrom. **9**, 453 (1995)