

Growth of organic thin films by the matrix assisted pulsed laser evaporation (MAPLE) technique

A. Piqué^{a,*}, R.A. McGill^a, D.B. Chrisey^a, D. Leonhardt^a, T.E. Mslna^{b,1}, B.J. Spargo^a,
J.H. Callahan^a, R.W. Vachet^a, R. Chung^b, M.A. Bucaro^a

^aNaval Research Laboratory, Washington, DC 20375, USA

^bGeo-Centers, Inc. Ft. Washington, MD 20744, USA

Abstract

A novel variation of conventional pulsed laser evaporation, known as matrix assisted pulsed laser evaporation, or MAPLE, has been successfully used to deposit highly uniform thin films of a variety of organic materials including a number of polymers. The MAPLE technique is carried out in a vacuum chamber and involves directing a pulsed laser beam ($\lambda = 193$ or 248 nm; fluence = 0.01 to 0.5 J/cm²) onto a frozen target (100 – 200 K) consisting of a solute polymeric or organic compound dissolved in a solvent matrix. The laser beam evaporates the surface layers of the target, with both solvent and solute molecules being released into the chamber. The volatile solvent is pumped away, whereas the polymer/organic molecules coat the substrate. Thin uniform films (< 50 nm) of various materials, such as functionalized polysiloxanes and carbohydrates, have been deposited on Si(111) and NaCl substrates. The films prepared using this method have been examined by optical microscopy, scanning electron microscopy, atomic force microscopy, Fourier transform infrared spectroscopy and electrospray mass spectrometry. Careful control of the processing conditions allowed the complex polymer/organic molecules to be transferred to the substrate as uniform films without any significant chemical modification. Using MAPLE, large or small regions within a substrate can be discretely coated with submonolayer thickness control. The use of MAPLE films for chemical sensor applications has been investigated and the potential of this technique for producing high quality thin films of other organic compounds will be discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Polymer thin films; Organic thin films; Chemical sensors; Matrix assisted pulsed laser evaporation

1. Introduction

Processing of polymer and organic (polymer/organic) thin films is of importance in a wide range of applications including electronics, non-linear optics and sensors. Thin polymer films can be deposited by a wide variety of techniques that range in their complexity and applicability. The choice of which deposition technique to use depends upon the physicochemical properties of the polymer, the requirements for film quality and the substrate that is being coated. The simplest methods involve the application of a liquid solution of a polymer in a volatile solvent, including: aerosol, dip and spin coating [1]. There are some techniques that are applicable to bulk polymer materials, including: vacuum evaporation [2] and pulsed laser evaporation or ablation [3–5]. Finally, there are techniques that involve in-situ polymerization of monomer using plasma [6], electrochemical

[7], catalytic, or photo-activated processes [8,9] to convert the starting material or monomer to a polymer on a substrate surface. For organic thin films, new techniques and methods have been developed for processing and characterizing these materials in thin film form, see for example the June 1995 and June 1997 issues of the MRS Bulletin [10]. However, each of the above mentioned techniques only work for certain types of compounds and are not generic enough to be used with a wide variety of polymer/organic materials to be deposited as thin, uniform and well adherent coatings over an extended substrate surface area, or in localized areas with accurate and precise thickness control, while maintaining their chemical integrity and desired physicochemical properties.

A new deposition technique, known as Matrix assisted pulsed laser evaporation (MAPLE), has been developed at the Naval Research Laboratories for depositing thin and uniform layers of chemoselective polymers [11–14], as well as organic compounds such as simple carbohydrates and their polymers [15]. MAPLE is a variation of the conventional pulsed laser evaporation (PLE) technique. It

* Corresponding author.

E-mail address: pique@nrl.navy.mil (A. Piqué)

¹ Present address: SRD Corp., P.O. Box 191, Orono, ME 04473, USA.

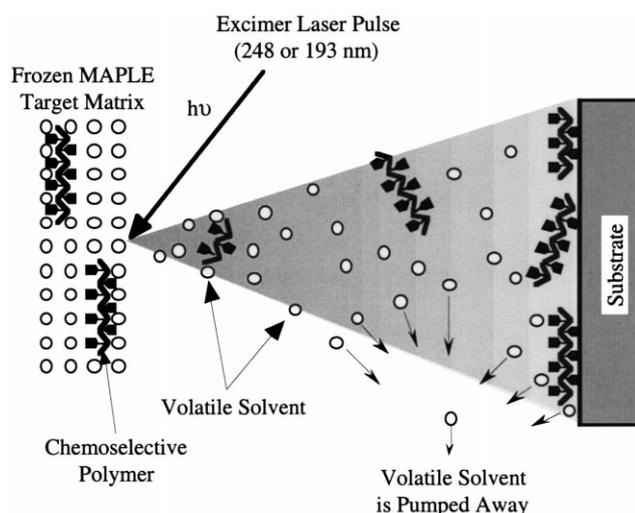


Fig. 1. Schematic of the MAPLE process.

provides a more gentle mechanism for transferring many different compounds that include small and large molecular weight species such as sugars and polymeric molecules, from the condensed phase into the vapor phase. In MAPLE, a frozen matrix consisting of a solution of a polymeric organic compound dissolved in a relatively volatile solvent is used as the laser target. The solvent and solution concentration are selected so that the polymer/organic of interest can dissolve to form a dilute, particulate free solution and also so that the majority of the laser energy is initially absorbed by the solvent molecules and not by the solute molecules. At a molecular level in a photothermal process, the absorption of photons by the frozen solvent molecules is converted to thermal energy which causes the polymer/organic to be heated but the solvent to vaporize. As the surface solvent molecules are evaporated into the gas phase, polymer/organic molecules are exposed at the gas-target matrix interface. The polymer/organic molecules attain sufficient kinetic energy through collective collisions with the evaporating solvent molecules, to be transferred into the gas phase. By careful optimization of the MAPLE deposition conditions this process can occur without any apparent polymer/organic decomposition. The MAPLE process proceeds layer-by-layer, depleting the target of solvent and polymer/organic material in the same concentration as the starting matrix. When a substrate is positioned directly in the path of the plume, a coating starts to form from the evaporated polymer/organic molecules, while the volatile solvent molecules, which have very low sticking coefficients, are evacuated by the pump in the deposition chamber, Fig. 1. The MAPLE technique is analogous to the analytical technique matrix assisted laser desorption/ionization-mass spectrometry (MALDI-MS)[16]. MALDI-MS is a soft ionization technique that allows the desorption and ionization of large molecular species ($\sim 10^4$ – 10^6 amu). This process has been developed for studying large organic molecules and polymeric materials to accurately determine

their molecular weight distributions. The main difference between the MAPLE and MALDI techniques lies in the treatment of the evaporated polymer/organic. In the MAPLE process the polymer/organic is not deliberately ionized and is collected on a substrate to form a coating rather than being directed into a mass spectrometer.

In this work, the MAPLE technique has been utilized successfully for depositing uniform thin films of fluoroalcoholpolysiloxane or SXFA, a chemoselective polymer for sensor applications and simple organic carbohydrate compounds of low and high molecular weight. The films were deposited on Si(111) and NaCl substrates under a variety of processing parameters. Fourier transform infrared spectrometry (FTIR) and electrospray mass spectrometry were utilized in order to confirm the chemical integrity of the coatings. The surface morphology of several of these films was evaluated using optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques.

2. Experimental details

The MAPLE deposition system, shown in Fig. 2, consisted of a pulsed laser deposition chamber with a modified substrate holder fixture that housed a surface acoustic wave (SAW) device and associated electronics. The SAW device was used to monitor the deposition rate during film growth, as previously reported [12]. The substrate holder was mounted parallel to the frozen MAPLE target surface. For a target to substrate distance of 5 cm, a region about 6 cm² was uniformly coated. Several 1 cm² Si(111) substrates together with one 1 cm diameter NaCl disc were coated in each run. The substrates were at room temperature during deposition.

A Lambda Physik LPX-305i Excimer laser operating with a KrF gas mixture (30 ns pulse length at 248 nm) or

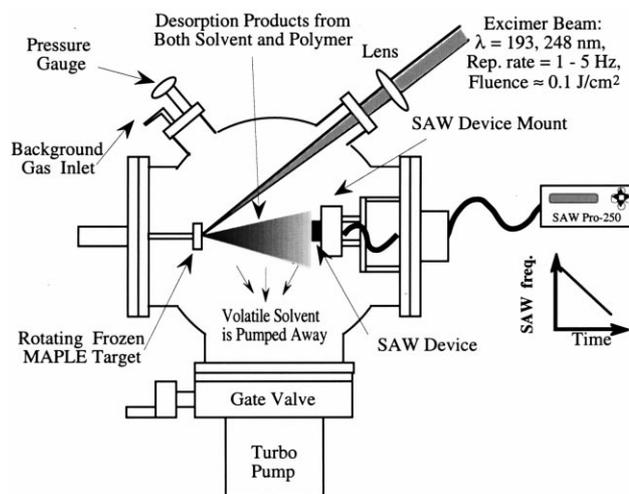


Fig. 2. Schematic of the MAPLE deposition system showing its main components.

Table 1
Processing conditions for MAPLE deposited thin films of chemoselective polymers and carbohydrates

Laser wavelength (nm)	248 or 193 for polymers 193 for carbohydrates
Laser power (W)	~ 0.02
Laser spot size on the target (cm ²)	~ 0.4 × 0.1
Laser fluence on the target (J/cm ²)	0.05–0.25
Laser repetition rate (Hz)	2–5
Target size (cm diameter)	~ 2.5
Target to substrate distance (cm)	5
Substrate type	NaCl, Si, Au/Si and quartz (SAW)
Substrate temperature (°C)	Room temperature (25)
System base pressure prior to deposition (Torr)	10 ⁻⁵
Background gas during deposition	Ar or Ar/H ₂
Background pressure during deposition (Torr)	5 × 10 ⁻² (50 mTorr)
Deposition rate (Å/laser pulse)	0.03–0.05
Typical film thickness (nm)	20–50
Typical deposition time (min)	20–50

an ArF mixture (20 ns pulse length at 193 nm) firing at rates between 1 to 5 Hz was used. The excimer laser beam was incident on the target at a 45° angle and was focused onto a spot 0.05 cm² in area. The laser fluence at the target was varied between 0.01 and 0.5 J/cm². The laser beam was rastered over the target surface while the target was rotated in order to avoid excessive heating and erosion of a single spot on the target that could lead to damage of the matrix surface. Prior to starting the deposition, the SAW device was turned on and a baseline signal frequency was established. During depositions, the SAW device frequency shift was monitored in order to follow the film growth rate. Films were deposited under Ar or Ar saturated with water vapor partial pressures totaling 50 mTorr. At the end of each deposition, the chamber was vented with dry nitrogen.

In order to deposit polymer films using the MAPLE technique, a matrix solution was prepared by dissolving SXFA in tert-butyl alcohol at a concentration of 0.005 g/g. For the carbohydrate films, the targets utilized consisted of matrix solutions of glucose, sucrose or dextran (average $M_w = 148\,000$ amu) dissolved in deionized water at 0.05 g/g. All the reagents were obtained from Sigma Chemical Co. and used without further processing, except for the SXFA polymer, which was synthesized at NRL [17]. In each case, the matrix was decanted into a 2.5 cm diameter × 1.0 cm deep Teflon coated target die. The die was cooled to -20°C in order to freeze the matrix solution. An open end of the die formed the MAPLE target. Before deposition, the frozen target was mounted on a brass holder and the whole assembly submerged in liquid nitrogen for about 5 min. Upon removal from the liquid nitrogen, the frozen MAPLE target was mounted inside the deposition chamber. This arrangement allowed the target to remain frozen for 2 h. This

provided enough time to evacuate the chamber to a base pressure of 1×10^{-5} Torr, introduce the background gas and perform the deposition. After each deposition the target was recovered for later use and stored in a refrigerator.

Using the above conditions, the deposition rate for the polymer/organic materials was measured at about 0.3 Å every 10 laser shots. In general, the film thickness was calculated from the shift in frequency measured for the SAW resonator [12]. Table 1 provides a list of the key deposition parameters utilized for growing polymer and organic thin films by the MAPLE technique.

The surface morphology of the films was evaluated using optical microscopy. Several SXFA films were coated with a 10 nm thick AuPd layer so that they could be examined using a LEO 400 series scanning electron microscope and a Digital Instruments Dimension 3000 atomic force microscope. The films grown on NaCl discs were analyzed using a Nicolet Magna-IR 750 Fourier transform infrared (FTIR) spectrophotometer in order to verify their chemical integrity. Using a Finnigan-Thermoquest LCQ ion trap mass spectrometer equipped with an electrospray interface, the mass spectra of the sugar and dextran films deposited on silicon were compared with the native materials. The samples were evaluated using a variation of electrospray known as nanospray, which offered the sensitivity required for detecting the small amounts of material present in the MAPLE films. NaCl was added to the solutions formed by washing the films off the substrates in order to promote the formation of ions for mass analysis.

3. Results and discussion

3.1. MAPLE of SXFA polymers

For chemical sensor applications, the physicochemical properties of the chemoselective coating are critical for the sensor performance [18]. One chemoselective polymer that has a variety of desirable properties is SXFA. The FTIR spectra of the material collected after PLE of SXFA (Fig. 3c) provides evidence for total decomposition. For other highly functionalized polymeric materials similar decompo-

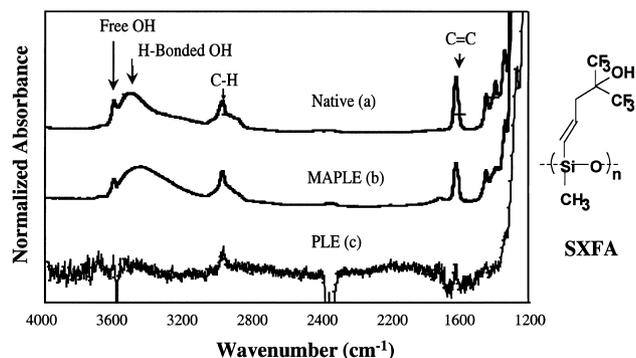


Fig. 3. FTIR spectra for (a) native SXFA, (b) material deposited by MAPLE and (c) material deposited by PLE.

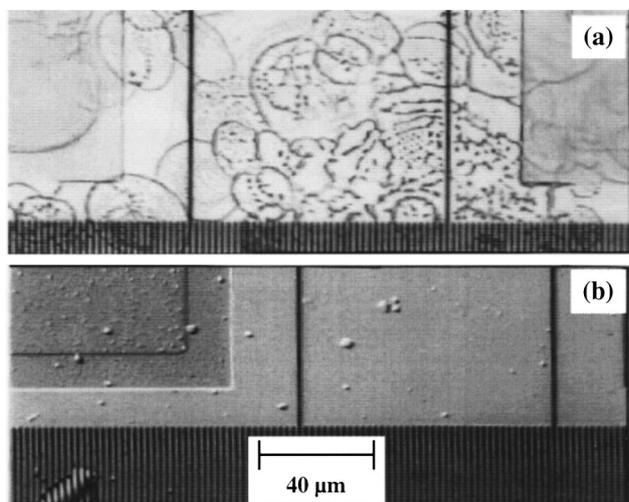


Fig. 4. Optical micrographs showing the surface of SAW devices coated with SXFA by (a) aerosol and (b) MAPLE.

sition trends were observed with major polymer decomposition [12,13]. Clearly for highly functionalized materials a more gentle process than conventional PLE is required for the coating deposition to proceed without significantly modifying the physicochemical properties of the starting material. The FTIR spectra of the native SXFA (Fig. 3a) and MAPLE coated SXFA (Fig. 3b) are essentially identical with very similar absorbance ratios for the key absorption bands. The MAPLE process is gentle enough to limit any polymer decomposition to a minimum.

The photomicrograph of SXFA coated by an aerosol (Fig. 4a) shows a non-uniform coating on a silica treated SAW device surface. The aerosol produces non-uniform coatings because the solvent evaporates in a non-uniform fashion. In contrast, the photomicrograph for the MAPLE coated SXFA (Fig. 4b) indicates that the coating is uniform with minor topographic features. SEM analysis of SXFA films deposited on (111) silicon substrates by aerosol and MAPLE revealed similar features as indicated by the images shown in Fig. 5. The surface morphology and RMS roughness of these films became was evaluated by AFM. Fig. 6 shows the AFM images ($35 \times 35 \mu\text{m}$) belonging to SXFA films aerosol and MAPLE deposited on silicon (111) substrates. The RMS surface roughness of the SXFA film coated by aerosol was $\sim 11.3 \text{ nm}$ compared with a value of $\sim 2.6 \text{ nm}$ for the SXFA film deposited by MAPLE. The AFM images confirm that the MAPLE deposited films have a surface quality superior to that of the aerosol coated. The MAPLE process allows a uniform deposition because when the polymer is deposited on a substrate the polymer is free of solvent.

3.2. MAPLE of carbohydrate molecules

Initial deposition tests were performed using the KrF excimer emission at 248 nm. At low laser fluences, using

this wavelength, no signs of film growth could be detected by the SAW device. Furthermore, the NaCl substrates used for these tests did not show any absorption bands when examined by FTIR. Only when fluences in excess of 1.0 J/cm^2 were utilized, it was possible to notice material accumulating on the surface of the SAW device and substrates. However, at such high fluences, the matrix target sustained considerable damage, as evidenced by the discoloration of its surface due to charring and the scattered debris on the films resulting from target spallation. This problem, which was caused by the poor coupling between the frozen matrix and the 248 nm laser pulse and was solved by using the ArF excimer emission at 193 nm.

At 193 nm, the coupling between the laser pulse and the aqueous MAPLE target was more efficient as demonstrated by the SAW resonator frequency response and the formation of visible steps within masked substrates. Films with relatively smooth and uniform surfaces were produced with fluences between 0.2 and 0.3 J/cm^2 . Under these conditions, the deposition rate was near 0.5 \AA every ten laser pulses. Increasing the laser fluence resulted in higher deposition rates at the expense of an increase of the film particle density. For fluences below 0.1 J/cm^2 , it became difficult to determine if any material was desorbed from the target.

In order to characterize the chemical structure of the deposited material, FTIR spectra of both films and their native counterparts were collected. In each case, the full

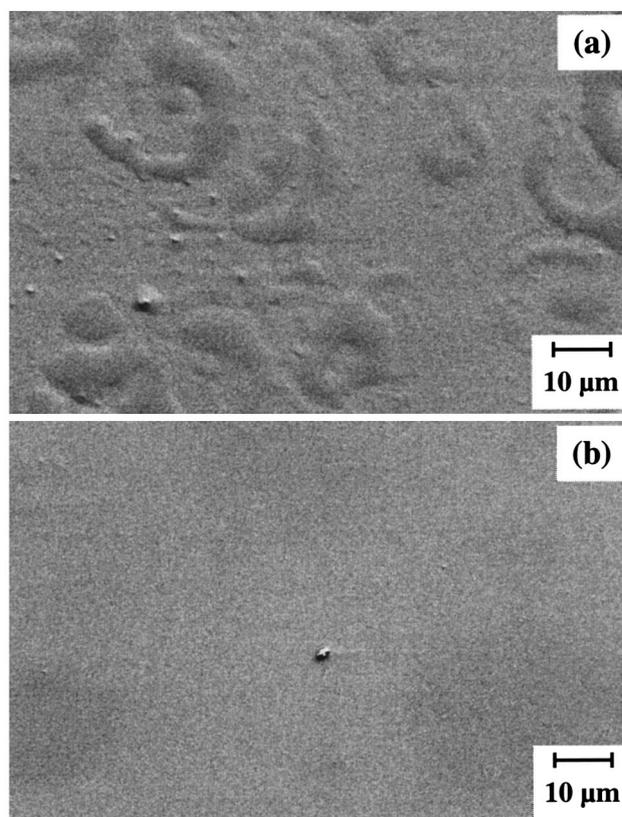


Fig. 5. SEM images of SXFA films on silicon substrates deposited by (a) aerosol and (b) MAPLE.

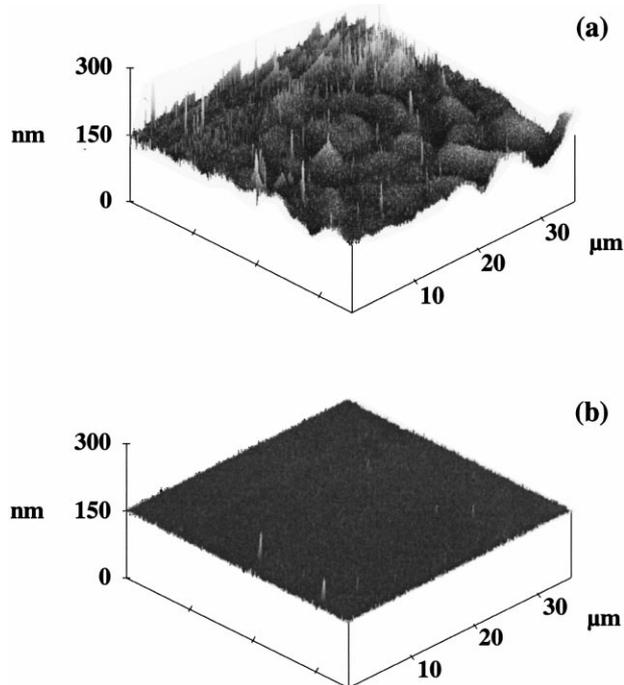


Fig. 6. AFM images of SXFA films on silicon substrates deposited by (a) aerosol and (b) MAPLE.

transmittance spectra showed the presence of the expected corresponding major and minor absorption bands. Furthermore, the transmittance ratios for different bands remain the same as for the corresponding native carbohydrate. Fig. 7 shows the spectra corresponding to the fingerprint and carboxyl stretching region for native carbohydrate samples and thin films produced by MAPLE of: (a) glucose, (b) sucrose and (c) dextran. For each of these spectra, the material collected in the films appears to be essentially identical to the native carbohydrate.

The effect of the background gas on the growth of carbohydrate films was also studied. FTIR spectra of the films deposited by MAPLE in a background pressure of Ar saturated with water vapor, instead of pure Ar gas, showed an increase in the absorption bands characteristic of the O–H stretch. These data suggest that the MAPLE technique might be useful for depositing thin films of organic hydrated compounds such as hydrogels. Thin films of hydrogel materials similar to those described in this work, can be used in applications such as biosensors and biofilms. In these cases, a highly hydrated surface or water retaining surface is required to support higher order macromolecular structures or allow diffusion of molecules such as analytes or nutrients for detection and metabolism, respectively.

Analysis by electrospray mass spectrometry provided information about the molecular weight of the material in the films made by MAPLE. Several glucose, sucrose and dextran films on Si substrates were analyzed and compared with samples of their native counterparts which were used as standards. For the glucose and sucrose films, no signs of fragmentation of the molecules present from the films

grown by MAPLE could be observed. As Fig. 8 indicates, the spectra for the glucose and sucrose films were essentially identical to that of the native material. The additional mass peak observed in the MAPLE sucrose spectrum is a result of a sucrose/NaCl cluster that forms from the nanospray process. However, the spectra from the dextran samples were more difficult to evaluate due to the large average molecular weight of the carboxyl dextran molecule ($\sim 148\,000$ amu). In this case, it appears that the average molecular weight of the dextran films is $\sim 70\,000$ amu and the low end of the molecular distribution extends below $19\,000$ amu. It is not yet clear if the fragmentation exhibited by the dextran molecules was caused during target preparation or during the MAPLE desorption process.

4. Summary

Highly uniform films of the chemoselective polymer SXFA and various carbohydrate materials were deposited

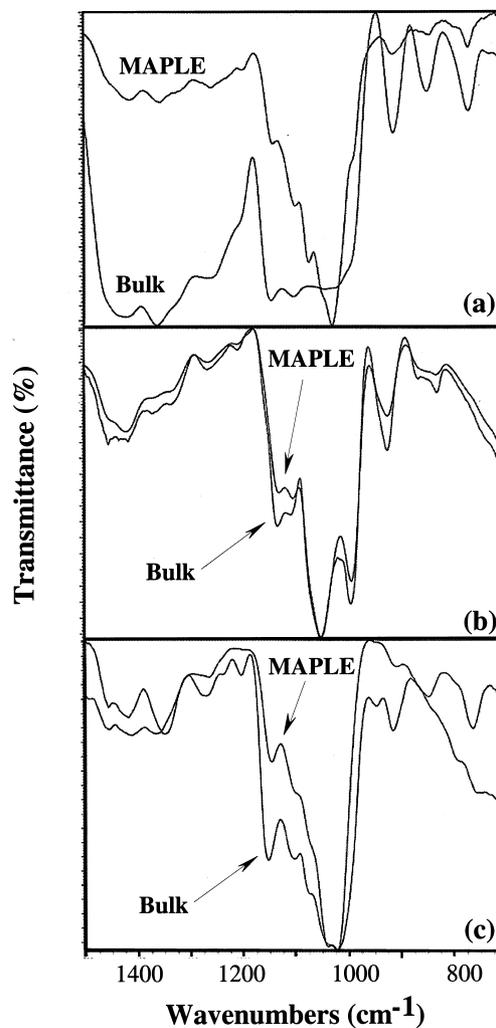


Fig. 7. FTIR spectra showing the carbohydrate fingerprint region from native and MAPLE samples of (a) glucose, (b) sucrose and (c) dextran.

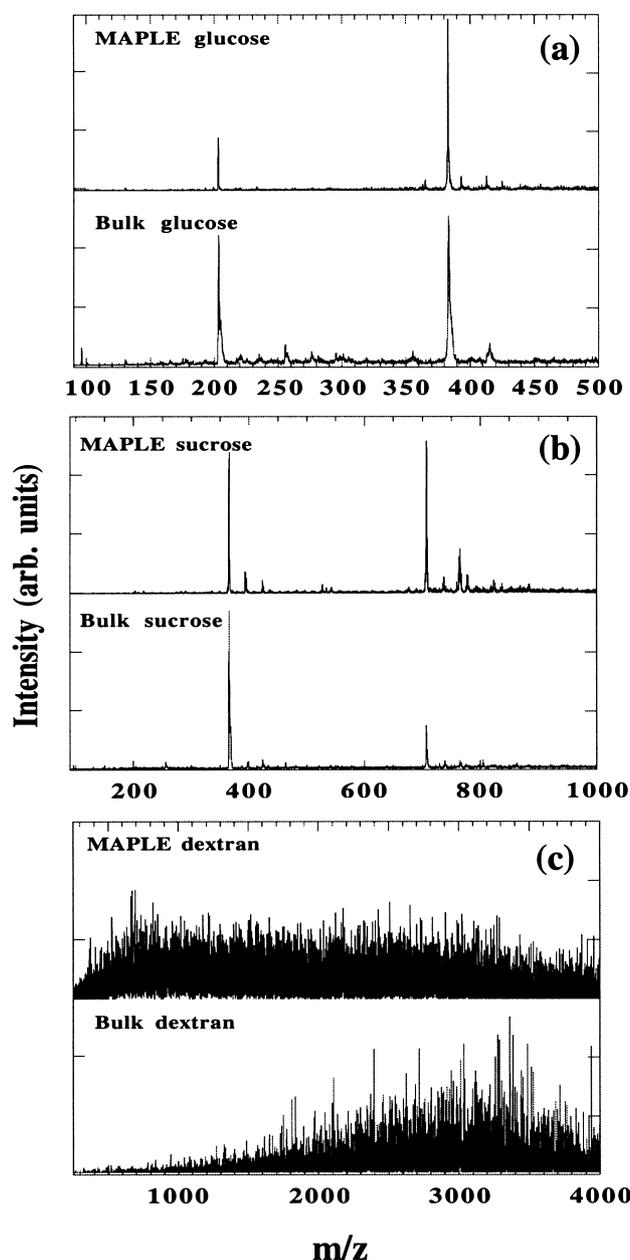


Fig. 8. Electrospray mass spectra of native and MAPLE samples of (a) glucose, (b) sucrose and (c) dextran.

in a photothermal process using a pulsed excimer laser fired at a frozen solute/solvent matrix target. When the matrix is hit with the laser pulse the solvent molecules impart sufficient kinetic energy to the solute polymer/organic molecules to lift them into the gas phase without any apparent decomposition. Comparison of the infrared spectrum of the native polymer with the coatings deposited by the PLE and MAPLE methods reveals major differences. The PLE results in complete decomposition while the MAPLE process deposits the polymer unchanged. The MAPLE coatings exhibit considerably less surface roughness than those

coatings from the more traditional aerosol coating methods. Thin films of glucose, sucrose and dextran were deposited using a frozen target made from an aqueous solution of each carbohydrate. The MAPLE process generated uniform coatings about 50 to 100 nm thick over Si and NaCl substrates. FTIR analysis of these organic films indicated that their chemistry was essentially identical to that of the native compounds. For the organic films, the molecular weight distribution of the material deposited was evaluated using electrospray mass spectrometry. The mass spectra of the glucose and sucrose films were very similar to that of the native sugars, while the dextran spectrum showed a lower average molecular weight than the bulk. In each case, the data demonstrate that MAPLE can be employed for the growth of high quality polymeric as well as organic thin films useful for a wide range of applications.

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