Matrix Assisted Laser Processing of Organic Thin Films with an Er:YAG Laser

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This work focuses on the deposition of organic thin films by matrix assisted pulsed laser deposition. In particular, an Er:YAG laser is used and the results compare more than favorably with those obtained when using an ArF (193 nm) laser. The deposition of polyethylene glycol, fluropolyol, polyaniline (emeraldine salt), and calf thymus DNA is reviewed and discussed.

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1. Introduction

There is a growing need for advanced laser processing thin film deposition techniques. In particular, laser deposition of organic thin films has received recent attention[1]. Pulsed laser deposition (PLD) stands out as a promising thin film processing technique; however, the laser-material interactions with soft matter such as polymers and other organics can be problematic. In PLD, it is typical to use UV lasers which can induce strong photochemical and photothermal interactions. There are a number of possible alternatives to conventional UV-PLD discussed in Ref. [1], here, we will focus on Matrix Assisted Pulsed Laser Evaporation (MAPLE) and related techniques. In MAPLE a material (guest) to be deposited as a thin film is placed in a host matrix, frozen, and flash evaporated (ablated) in a vacuum chamber. In the most optimistic scenario, the host absorbs the laser light and the guest is gently desorbed from the target and lands on the substrate where it forms a thin film.

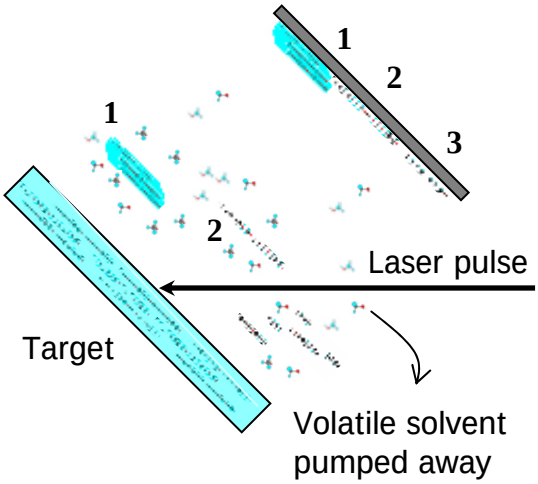

Figure 1 - Schematic of the MAPLE process. Events 1, 2, and 3 are discussed in the text

Figure 1 displays a schematic of the MAPLE process. We have chosen to highlight three possible outcomes out of many possibilities. In the first, a 'chunk' of the target is removed by the laser pulse and lands nearly intact on the substrate. Presumably, it will melt on the substrate and it solvent will evaporate, possibly creating a 'wicking' effect. In the second case, a polymer chain is desorbed whole and lands on the substrate, adding to the film one layer at a time. This is what we referred to previously as the most optimistic case. In the third case, the guest molecule is fragmented and the film will be composed of modified oligomeric fragments. In addition to ours, a number of groups are undergoing experimental[2] and computational[3] investigations of MAPLE in order to determine the primary mechanisms of ejection and the relevance of the processes shown in Figure 1.

In this work, we focus on the use of an Er:YAG laser as the excitation source in MAPLE. It emits light at 2.94 μm (3401 cm^{-1}) which is resonant with the –OH stretch in water and alcohols as well as the amide stretch in solvents like formamide. The use of an IR laser may present certain advantages over UV lasers during MAPLE, since a large number of photons will be required in order to initiate photochemical processes. Although the absorption coefficient of water drops off to about 3000 cm^{-1} at moderate radiant exposures[4], this should still be enough to reach energy densities on the order of kJ/cm^3, which are required for ablation. It should be noted that we are actually interested in the penetration depth for ice, which has a similar absorption coefficient to water in the 3 μm region[5], but no study exists that we are aware of which dynamically probes for changes in the absorption spectrum of ice under radiant exposures of ~ 1-10 J/cm^2. Studies of laser resonant desorption of ice with an Er:YAG laser show that it takes about 6-7 laser pulses to remove a 3 μm thick film [6]. Therefore, we conservatively estimate the penetration depth of the Er:YAG laser light be between 0.5

and 1 μm. Therefore for a fluence range of 5 – 10 J/cm^2, energy densities between 50 - 100 kJ/cm^3 are reached.

2. Previous MAPLE Results – Avoiding Photochemistry

Previous work has focused on comparing UV-MAPLE with an ArF laser (193 nm) with both H_2O and $CHCl_3$ as matrices[7]. Cl radicals and other reactive species were detected during quadrupole mass spectroscopy experiments when ablating frozen $CHCl_3$ targets with an ArF laser. In contrast, the same experiments with ice suggested that H_2O was not photo-dissociating. When the deposited films of polyethylene glycol were characterized, the $CHCl_3$-deposited films showed clear evidence of alteration with respect to the starting material in the infrared spectra. In contrast, the films that were deposited using ice as a matrix appeared very similar to the starting material. In Fig. 2, we show the infrared spectra of polyethylene glycol films deposited by MAPLE using both H_2O and $CHCl_3$ matrices. The interpretation of these results is that MAPLE is a process which has the best chance of success if the production of reactive species can be kept to a minimum.

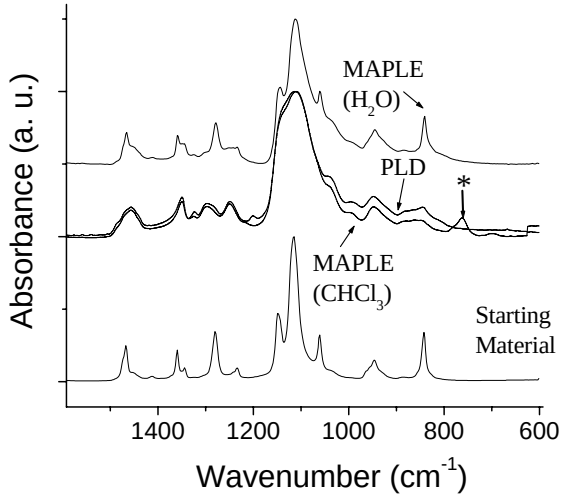

Figure 2 - Inset of Fig. 1 in Ref. [7]. The infrared spectra of the starting material and MAPLE deposited films are shown. For comparison, a film deposited by conventional UV-PLD at 193 nm is shown. Note its similarity to the film deposited using $CHCl_3$ as a matrix.

One possible way to minimize photochemical interactions is to change the wavelength of the laser. Fluoropolyol, a sorbent, chemoselective, oligomer was deposited by MAPLE using an Er:YAG laser and a ArF laser[8]. Alcohols such as t-butanol and methanol were used as matrices. The UV-MAPLE deposited films were significantly altered with respect to their physicochemical structure in comparison with the Er:YAG deposited films as determined by infrared spectroscopy and electrospray ionization mass spectrometry. This points to another potential problem with UV-MAPLE; even if the solvent matrix does not produce reactive species when ablated, the polymer itself may contain strongly UV absorbing moieties that could conceivably cause more absorption by the guest molecules than the host to occur in the target. Size exclusion chromatograms are displayed in Fig. 3 of the UV-MAPLE and IR-MAPLE deposited films compared with the starting material. The UV-MAPLE elutes at a larger volume, and hence, is reduced in size in comparison with the starting material and IR-MAPLE films. There is significant modification of the UV-MAPLE film's infrared spectrum in the fingerprint region as well. We believe these results highlight the utility of IR-MAPLE. The next challenge in the development of this technique will be controlling the morphology and beginning to answer the questions posed in Figure 1.

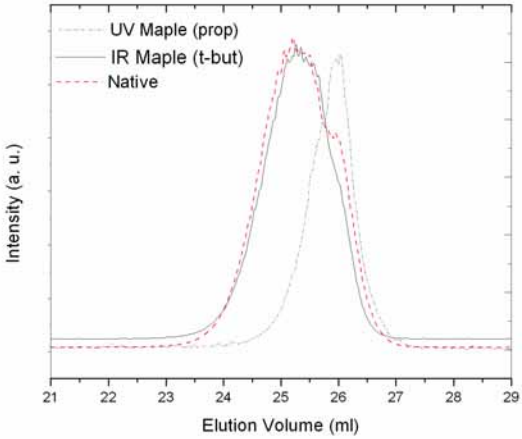

Figure 3 - Size exclusions chromatograms of native fluoropolyol and MAPLE Films

3. Intermediate between MAPLE and PLD: the deposition of polyaniline

Polyaniline is a conducting polymer that has a number of exciting potential applications[9,10]. The main challenge to its effective use is that it is difficult to process; in particular, the conducting form is insoluble in conventional solvents. Attempts were unsuccessful to use resonant infrared pulsed laser deposition (RIR-PLD) in order to deposit the films. Strong visible emission was observed during the deposition process and the films were not conducting[11]. Next, polyaniline was dispersed in methanol and the target was frozen as in a regular MAPLE experiment with the Er:YAG laser.

Here, we found that films of 3-5 μm thickness could be

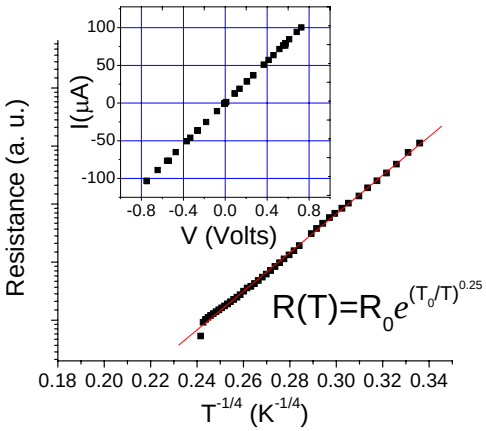

Figure 4 - Resistance vs. temperature of thin film of polyaniline. The inset shows the ohmicity of the contacts.

deposited. The films are conducting and reflect all of the spectral properties of the conducting salt of polyaniline. The conductivity of the films were measured and found to be ~2-5 S/cm which is very similar to the bulk material. The film's resistance vs. temperature curve was measured and found to be consistent with Mott variable range hopping[12] in three dimensions. These results demonstrate that polyaniline was successfully deposited in the emeraldine salt form. The significance of this result is that it shows that MAPLE can be extended to cases in which the guest is not soluble in the host. It represents an intermediate case between IR-MAPLE and RIR-PLD and further illustrates the utility of matrix assisted laser processing techniques.

4. Laser Deposition of Calf Thymus DNA

There is a high level of interest in using thin films of large organic molecules such as DNA as the active element in sensors. One such example uses calf thymus DNA immobilized on electrodes in order to detect pollutants[13]. Previous work has been done with IR-MAPLE of salmon

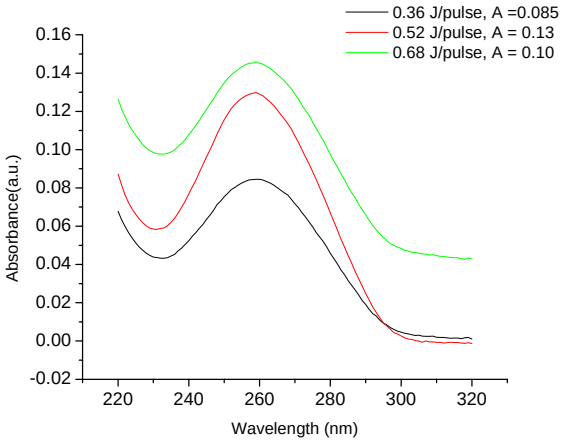

Figure 5 - UV spectra on three calf thymus DNA films deposited at differing pulse energies

sperm DNA and pBluescript DNA[14]. Here, we describe the deposition and characterization of laser-deposited calf thymus DNA.

Highly polymerized fibrous calf thymus DNA was purchased from Sigma-Aldrich (D-1501) and reconstituted in 10 mM potassium phosphate buffer (pH=7.0, 1 mM EDTA, 100mM K^+). The concentration of DNA in the MAPLE solutions varied from 0.47 to 1.88 mg/ml. The depositions were carried out in a vacuum chamber that was kept at a pressure below 10 mTorr. The spot size was between 0.042 and 0.063 cm^2, yielding a fluence range from 8.6 to 10.8 J/ cm^2.

We have characterized the deposited films with UV and circular dichroism (CD) spectroscopy. In addition gel electrophoresis was performed in order to determine if the DNA has been fragmented.

The UV spectra of films deposited at three different laser energies are shown in Figure 5. The concentration of the MAPLE solution was 0.47 mg/ml. 20,000 laser pulses were used to deposit each film. It is interesting to note that at the highest energy (0.68), the absorbance (difference between absorbance at 260 nm and 320 nm), and hence the deposition rate is lower than that at 0.52 J/pulse. There are a number of possible reasons for this. It may be that we are destroying some of the DNA when the laser is operated at the highest pulse energies. We think that this is unlikely for reasons that are demonstrated in the coming paragraphs. Another possibility is that the shape of the plume changes with increasing fluence in such a way as to reduce he deposition rate. However, at this point, the reasons why the deposition rate is lower at 0.68 J/pulse as compared with 0.52 are uncertain, and are the subject of further investigation.

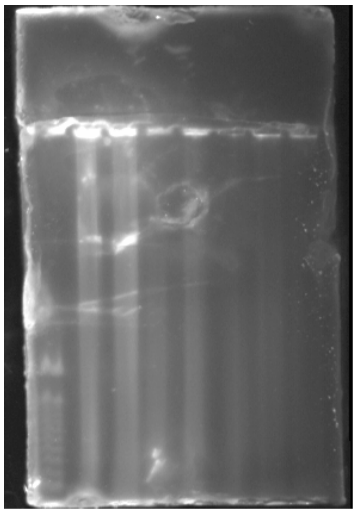

Figure 6 - Gel Electrophoresis of DNA Films. There are eight wells. The leftmost well contains a molecular ladder. The second well contains native Calf Thymus DNA and the rest are from deposited films.

Next, we deposited six films with varying pulse energies (0.36, 0.52, 0.68 J/pulse) and solution concentrations of 0.47, 0.94, and 1.41 mg/ml. The films that were deposited with solutions of different concentrations were done at a laser energy of 0.68 J/pulse. They were deposited on sodium silicate glass microscope slides and washed off in buffer solution after deposition. The DNA was extracted from solution and it was placed in 10 ul of a solution containing dye (Xylene-Cyanol Blue 1X TBE) and injected into one of eight wells in a 1% agarose gel. The results, shown in Figure 6, clearly show that the DNA has not been fragmented in the deposition. If fragmentation occurred, bright banding would be seen in intermediate positions throughout the gel. In contrast, our DNA samples remained localized in their respective wells, thus indicating that they had not been appreciably reduced in size. The first (leftmost) well contains a molecular weight ladder. Next is the native Calf Thymus DNA. The remaining 6 wells are populated with DNA that had been extracted from deposited films.

UV Circular dichroism measurements were performed in order to verify the structure and conformation of the deposited DNA films. In Figure 7, the native DNA's spectrum is compared to that of a film deposited with a pulse energy of 0.36 J. After deposition, the films were

washed off in using 1 ml of the aforementioned 10 mM potassium phosphate buffer.

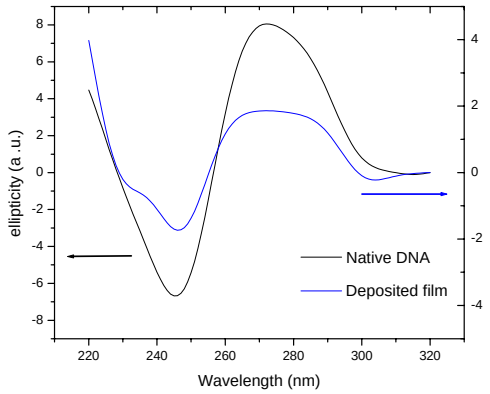

Figure 7 – UV CD spectra of native Calf Thymus DNA and a deposited film

Examination of Figure 7 shows that the spectra are clearly that of B-type DNA[15]. The peak at around 270 nm, followed by a valley at around 240 nm is the signature of this structure. Given our results, we feel confident in asserting that both the primary and secondary structures are preserved in the deposition process. This is a crucial point in the development of sensors.

In Figure 8, we compare the CD spectra of films deposited at three different pulse energies. Although there is some variation in the individual spectra, they are all characteristic of B type DNA. Our future work will focus on DNA with a better defined and narrower molecular weight distribution such as t4G4. In addition, this type of DNA forms a quadruplex structure that will be a challenge to preserve.

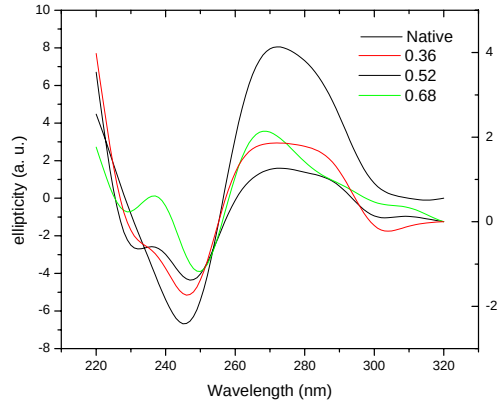

Figure 8 – UV CD spectra of Native Calf Thymus DNA and three films deposited at differing laser pulse energies

5. Concluding Remarks

In this paper, matrix assisted laser deposition of organic films of three distinct types has been discussed. An Er:YAG laser has been used for the depositions and it is believed to have certain advantages over UV lasers. The low photon energy coupled with the fact that this wavelength is strongly absorbed by matrices such as water and alcohols makes the Er:YAG a natural choice for thin film deposition experiments.

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