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Thin films growth parameters in MAPLE; application to fibrinogen

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Abstract. Increasingly requirements on the thin film quality of functionalized materials are efficiently met by a novel laser processing technique – Matrix Assisted Pulsed Laser Evaporation (MAPLE). Examples of deposition conditions and main features characteristic to film growth rate of MAPLE-fabricated organic materials are summarized. MAPLE experimental results are compared with ones corresponding to the classical Pulsed Laser Deposition (PLD). In particular, the results of investigation of MAPLE-deposited fibrinogen blood protein thin films using a KrF* excimer laser and characterized by FTIR and Raman spectrometry are reported.

1. Introduction
Recently, great interest in producing thin, high quality, uniform, and adherent coatings of functionalized materials, without damage to their structure or effect on their chemical or, biological activity, has been demonstrated. These properties are mandatory for a wide variety of specific applications from electronics to drug delivery and medicine. Functionalized materials include a large class of materials that range from inorganics and simple polymers to enzymes, active proteins, antibodies, nucleic acids and living cells. A very important difference between biomaterials and passive materials, such as dielectrics, is their activity, i.e. they have specific biochemical function. This implies that biomaterial transfer requires preserving molecular functions. Because in the case of functionalized materials the chemical bonds have assigned energies well below those corresponding to UV photon energies, some degree of photochemical decomposition is expected during Pulsed Laser Deposition (PLD) processing [1]. New attractive solutions of this problem have emerged: UV Matrix Assisted Pulsed Laser Evaporation (UV-MAPLE) [2]. Resonant Infrared-PLD (RIR-PLD) [3] or their combination RIR-MAPLE [4].

In PLD, the laser is used for ablation of bulk material, which is then collected on the substrate. RIR-PLD differs from PLD in using of an IR laser tuned to be resonant with a specific bond
wavelength of the molecule. In this case, the result is a non-destructive gentle evaporation even for large molecules. The main shortcoming of this method is the need for using an infrared laser, which must be tuned to a characteristic wavelength such as free electron laser (which is tunable from 2 to 10 μm [3-5]) or Er:YAG (2940 nm), which is efficient for alcohol as a matrix [6]. In principle, MAPLE is very similar to PLD. It deviates from PLD by target preparation and deposition conditions, such as laser fluence. The frozen target (from 77 K to 240 K) consists of solute functionalized compound dissolved at low concentration (0.05 - 5 wt. %), in a volatile solvent (consequently the word “matrix”) that in the ideal case strongly absorbs at laser wavelength. The beam energy is mainly absorbed by the matrix and the material is softly ejected from the target and carried towards the substrate while the solvent is pumped away and layers composed of large molecules are grown. Another reason why the solvent is not deposited is the “plume sharpening effect” [7]. This behavior known from matrix assisted laser desorption ionization mass spectrometry (MALDI-MS) has been demonstrated in case of heavier molecules of functionalized materials where the angular distribution of the plume is narrower than that corresponding to the lighter solvent (matrix) [8]. Fibrinogen is the large protein (molecular weight of 340 kDa) synthesized by the liver that occurs in blood plasma and which becomes transformed into a fibrin clot when activated by the enzyme thrombin. To investigate the level of fibrinogen these proteins must be transferred onto assays for further structural and morphological examinations as fast as possible. A fibrinogen assay measures the concentration of fibrinogen in the blood and may be used to evaluate abnormal blood clotting.

We review relevant data about the growth dynamic of UV- and RIR-MAPLE deposited thin films. Also deposition details on fibrinogen, including films characterization, are given.

2. MAPLE growth rate
The PLD growth rate (nm/pulse) is influenced by laser intensity incident on target, spot size, target-substrate distance, ambient atmosphere, optical and mechanical properties of target, substrate temperature and target-substrate-laser beam geometrical configuration. Typical PLD deposition rate is about 1 nm/pulse [1]. In MAPLE additional parameters such as properties of solvent, concentration of material and target temperature are necessary to be taken into account.

A comparison between MAPLE and PLD deposited thin films performed under nearly identical experimental conditions shows that MAPLE is about 4-8 times slower than PLD [9]. It has been shown that in both cases (PLD, MAPLE), the growth rate increases roughly as $d^2$ with decreasing target-to-substrate distance [10]. The laser fluence in MAPLE is very low, compared to PLD, where typically 2 J/cm$^2$ are applied (up to 33 J/cm$^2$ [11]), because the high fluence usually causes degradation of deposited material. On the other hand an important parameter is the ablation threshold that corresponds to a value after which the amount of ejected material from the target rapidly grows [12]. This has been observed as a minimal fluence, which is necessary for deposition [13]. The simplest way to create a usable target from a solution is to freeze it below the solvent melting point. The liquid nitrogen is frequently used as a medium, but when temperature going from 223 K to 113 K the growth rate is dropping 3−5 times [9]. Another important growth rate parameter is concentration of the material in solution. Recent studies [14, 15] showed that in the range from 0.5 to 4 wt. % the yield is linear proportional to the material concentration, but it is necessary to take into consideration the very high fluence value used to compensate low absorption of the solvent at the laser wavelength. This reveals one of the main issues of MAPLE: finding the proper solvent suitable for material and laser. The material absorption at the incident laser wavelength could influence the growth rate in a critical way.

We collected deposition data concerning MAPLE deposition, but most experiments are focused on the quality of deposited films rather than on film growth rate. The articles where the growth rate was directly reported or where we were able to calculate it are summarized in Table 1. We notice that the MAPLE growth rate ranges from 0.0005 nm/pulse to 1.1 nm/pulse. The value of 1.1 nm/pulse is quite high for MAPLE, because usually the growth rate does not exceed 0.2 nm/pulse. The deposition rate
for RIR-PLD and RIR-MAPLE is approximately the same (about 1.0 nm/shot) [3, 23]. It is higher due to the better efficiency of energy transfer between laser pulse and material.

We can conclude that MAPLE is less efficient and more expensive than conventional PLD at least from the point of view of the growth rate. However, we present an example that in our opinion demonstrates the reasons to further apply and develop the MAPLE technique for deposition of an important class of functionalized materials. This is the unique capability of MAPLE to preserve the starting composition and structure of any material including biomaterials with delicate large molecules. To this aim we first conducted experiments with fibrinogen and we further give convincing results in support of these capability and performances [24].

Table 1. Summary of deposition conditions and film growth rate for various experiments using MAPLE and RIR-MAPLE technique * = mg/ml, PhNi – Nickel(I) Phtalocyanine, CuTTP – Tetraethylporphyrin Cu(II), PhCo – Cobalt Phtalocyanine, DME – dimethoxy-ethane, DMSO – dimethyl sulfoxide, SXFA – polysiloxane, HRP – horseradish peroxidase, PEG – polyethylene glycol, DOPA – 3,4-dihydroxyphenyl-l-alanine, InAcAc – Indium acetyl acetone, Mn12-acetate – Mn12O12(CH3COO)16(H2O)4·2CH3COOH·4H2O, PBS – phosphate buffer solution, PLA–PGA – poly(d,l-lactide-co-glycolid), P3HT – poly(3-hexylthiophene), LN – liquid nitrogen temperature, N/A – not available.

| Material          | Solvent          | Concentration (wt%) | Fluence [J/cm²] | dts [cm] | Laser spot [mm²] | Laser wavelength [nm] | Pressure [Pa] | Target temperature [K] | Growth rate [Å/shot] | Ref |
|-------------------|------------------|---------------------|-----------------|---------|------------------|-----------------------|---------------|------------------------|----------------------|-----|
| fibrinogen        | physiologic serum| 0.32-0.68*          | 0.1-0.4         | 3       | 30               | 248, KrF              | 5-15, N₂      | 103                    | 0.01-1.93            | This work |
| cryoglobulin      | blood plasma     | 0.03-0.029*         | 0.3             | 3       | 10x3             | 248, KrF              | 10*          | 103                    | 0.15-1.21            | 27  |
| triacetate-pullulan| CHCl₃            | 2                   | 0.1-0.5         | 3       | 20               | 248, KrF              | 10*          | 103                    | 0.03-11.12           | 28  |
| InAcAc            | acetone          | 5                   | 0.07-0.15       | 3       | 20               | 248, KrF              | 3, N₂        | 103                    | 0.06-0.69            | 29  |
| PhNi              | DMSO             | 0.15-0.5            | 3               | 20      | 248, KrF          | 3, N₂                | 103          | 0.02-0.58              | 0.03-0.58            | 30  |
| CuTTP             | CHCl₃            | 0.10-0.2            | 3               | 20      | 248, KrF          | 3, N₂                | 103          | 0.11-0.30              | 0.03-0.58            | 30  |
| CuTTP             | CHCl₃            | 0.05-0.1            | 5               | 20/40   | 248, KrF          | 3, N₂                | 103          | 0.12-0.10             | 0.061/0.54           | 30  |
| PPhCo             | DMSO             | 0.30/0.5            | 3               | 20      | 248, KrF          | 3, N₂                | 103          | 2.06-1.54             | 0.01-0.54            | 30  |
| SXFA              | CHCl₃            | 0.5                 | 0.1-0.2         | 4       | 20               | 193, AsF              | 0.1-1.67, N₂  | 163-183                | 0.05               | 16  |
| Mn12-acetate      | 3-butanol        | 0.8-1.8             | 5               | 25      | 248, KrF          | 0.13-13              | LN           | 0.01-0.03              | 0.01-0.03            | 17  |
| Rut(bpyPMMA)₂(PF₆)₂| DME              | 2                   | 0.04            | 248, KrF      | 26.6, Ar      | LN                     | 0.005-0.03   | 18  |
| PEG               | CHCl₃ / H₂O      | 0.22-0.23           | 3               | 3.6     | 193, AsF          | 10⁻⁵ x 10⁴        | 113-223      | 0.1-0.21              | 9     |
| glucose, sucrose, | dextran          | H₂O                 | 0.05-0.25       | 5       | 4                 | 193, AsF              | 6.6, Ar      | LN                     | 0.05               | 13  |
| SXFA              | 3-butanol        | 0.2                 | 0.2-0.3         | 5       | 4                 | 248, KrF              | 6.6, Ar      | LN                     | 0.03               | 13  |
| HRP               | PBS              | 0.5                 | 0.1-0.2         | 3-7     | 193, AsF          | 10⁻⁵ x 10⁻³       | 113-233      | 0.2-0.6               | 10               |
| PGA - PLA         | ethyl acetate    | 0.96                | 0.165           | 7       | 5-10              | 193, AsF              | 10*          | LN                     | 0.024              | 19  |
| PEG               | H₂O              | 0.5-4               | 2.5-10          | 6       | 0.8-2.5           | 355, NdYAG          | 10⁴          | 223                   | 0.06-0.29            | 14,15,31 |
| modified DOPA     | H₂O              | 2                   | 0.41-0.62       | 2       | 25-3.5            | 193, AsF              | 10⁴          | 173                   | 0.03-0.05            | 20,21 |
| PSHT              | orthoxylene      | 0.8                 | 0.2             | 3.5-4   | 2-3               | 266, NdYAG           | 10⁻⁷ x 10⁻²   | 203                   | 0.009-0.05           | 22  |
| Fluoropolyol      | alcohol          | 15-20               | 3                | 9       | 2940, ErYAG       | <0.06              | -            | 10                     | 6     |
| Fluoropolyol      | 3-butanol        | N/A                 | 0.16             | 5.6     | 6                 | 193, AsF              | -            | 100                   | 0.01               | 6   |

3. Fibrinogen deposition
A crucial condition for proper evaluation of fibrinogen level is clean and accurate sample manipulation. This prerequisite is successfully met by laser processing.

We used fibrinogen collected from patients of Longhin Scarlat Dermato-Venerologic Hospital, Bucharest, Romania. At room temperature, a 2% concentration solution was obtained by dissolving the fibrinogen in physiological serum. The resulting solution was introduced in a copper cup and frozen at the liquid nitrogen temperature. Films were grown by MAPLE arrangement at the IP ASCR, Prague (KrF excimer laser, rotated target holder -cooled to LN temperature). Deposition conditions are included in Table 1. Films were characterized by FTIR (Thermo Nicolet Nexus 870) and by Raman spectroscopy (Renishaw Ramanscope, model 100), using Ar ion laser (514.5 nm) and by He-Ne laser (633 nm).

In figure 1, we give typical reflectance FTIR spectra recorded for the starting material as dropcast and for the MAPLE obtained thin films at a fluence of (a) 0.2 J/cm², (b) 0.3 J/cm², (c) 0.5 J/cm². We distinguished in our spectra several characteristic bands. A strong absorption is indicative of the band...
centered at 3295 cm⁻¹ due to C–H and N–H stretching mode. The band centered at 1655 cm⁻¹ is assigned to –C O amide carbonyl group the fingerprint for a large class of proteins: fibrinogen, collagen, fibronectin, and vitronectin. The band centered at 1544 cm⁻¹ is assigned to –C(O) stretching in aliphatic secondary amide. The typical band for fibrin formation by polymerization of fibrinogen 1150–980 cm⁻¹ is assigned to C–N stretching in aliphatic amides. This band results from lateral bonds which are secondary interactions that allow the material to form random coils. From figure 1, we notice that the spectra of samples deposited at fluence of 0.5 Jcm⁻² were the closest to dropcast spectra. Under these conditions we decided to continue investigations on the thin films deposited at the fluence of 0.5 Jcm⁻².

The Raman spectra of the fibrinogen dropcast and thin films obtained by MAPLE at 0.5 Jcm⁻² are shown in figure 2. The spectrum of fibrinogen dropcast shows several narrow characteristic peaks. Two peaks are relevant: the peak at 1450 cm⁻¹ and ~2930 cm⁻¹. One important observation concerns the similar structure of MAPLE deposited thin films as compared to the starting material [26].

Figure 1. Typical Fourier transform reflectance infrared spectra of fibrinogen for the starting material (dropcast) and thin films obtained by MAPLE at a fluence of: (a) 0.2 J/cm², (b) 0.3 J/cm², (c) 0.5 J/cm²

Figure 2. Raman spectra of fibrinogen layer fabricated at fluence of 0.5 Jcm⁻² (excitation at 633 nm) and dropcast (excitation at 633 nm and 514 nm).
4. Conclusion

From summarized experimental data we can conclude that the growth rate in MAPLE is lower compared to PLD. From experiments we determine that the MAPLE growth rate ranges from 0.001 nm/pulse to 1.1 nm/pulse. The material absorption at the incident laser wavelength could influence the growth rate in a critical way.

Further, we demonstrate in this work that MAPLE is suitable for producing fibrinogen thin films with close resemblance of the starting fibrinogen structure. We revealed by FTIR that spectra of samples deposited at fluence of 0.5 J/cm² were the closest to dropcast spectra. The Raman spectra show two narrow characteristic peaks at 1450 cm⁻¹ and ~2930 cm⁻¹.

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