Water ice as a matrix for film production by matrix-assisted pulsed laser evaporation (MAPLE)

K Rodrigo¹², J Schou¹, B Toftmann¹ and R Pedrys²

¹Department of Optics and Plasma Research, Risø National Laboratory, DK-4000 Roskilde, Denmark  ² Institute of Physics, Jagiellonian University, PL-30059 Krakow, Poland.

E-mail: j.schou@risoe.dk

Abstract. We have studied water ice as a matrix for the production of PEG (polyethylene glycol) films by MAPLE at 355 nm. The deposition rate is small compared with other matrices typically used in MAPLE, but the deposition of photofragments from the matrix can be avoided. At temperatures above −50 °C of the target holder the deposition rate increases strongly, but the evaporation pressure in the MAPLE chamber also increases drastically.

1. Introduction

It has recently been demonstrated that films of polymers or biomaterial can be produced by a technique, known as matrix-assisted pulsed laser evaporation (MAPLE). In MAPLE a guest molecule, e.g. a polymer, usually with a concentration of 0.1-2 wt. % is dissolved and subsequently frozen into a light absorbing matrix. When the matrix is irradiated by laser light, the solvent evaporates whereas the guest molecules are collected as a deposit on a substrate [1-4].

Water ice is perhaps the most versatile and convenient matrix for polymer and bioorganic materials. In principle, any non-volatile organic guest molecule which can be dissolved in water, is a possible film material, and a frozen aqueous solution has turned out recently to be an appropriate matrix for protein transfer to selected substrates [4,5]. We have systematically explored the possibility of using water ice as a matrix for the polymer, polyethylene glycol (PEG) in MAPLE [6-9]. A successful film deposition with MAPLE requires a highly absorbing matrix and a relatively low absorption by the guest material. It is also important that photochemical reactions between the matrix and guest materials can be avoided or considerably reduced [10]. In general, these requirements are difficult to fulfill completely.

PEG is a biotechnically important material [11], but has also become a model material for MAPLE. In the present work we have explored how efficiently water ice works as a matrix for laser irradiation at 355 nm, and to which degree photodecomposition of the matrix molecules influences the quality of the deposit for a variety of matrices. A significant deposition of PEG from water ice matrices requires at least a fluence in the range 2.5 – 5 J/cm², which leads to a strongly nonlinear absorption accompanied by emission of ions from the matrix [6]. Nevertheless, it was shown that the deposited material predominantly has the same mass distribution as the original polymer [7]. The deposition of protein films was carried out by Ringeisen et al. [5] at a very low fluence, less than 0.2 J/cm², but at the considerably shorter wavelength of 193 nm.
We have compared film deposition with four typical MAPLE solvents, water, isopropanol, acetone and toluene. It turns out that the water ice leads to the lowest deposition rate, but also that there are no decomposition fragments of the matrix molecules in the deposit for water ice. The target temperature is an important parameter for the deposition, and the deposition rate is strongly enhanced for temperatures of water ice close to the freezing point.

2. Experiments
The experiments have been carried out at the MAPLE setup at Risø National Laboratory. The setup was described in great detail in refs [6-9], and only a brief description will be given here. A laser beam at 355 nm was directed at an angle of 45° with respect to the normal onto a rotating ice target in a chamber with a base pressure of $10^{-6}$ mbar. The duration of the laser pulse was 6 ns and the fluence was varied between 2 and 10 J/cm². The area of the elliptical laser beam spot ranged from 0.008 cm² to 0.025 cm².

The target was a flash-frozen ice matrix made from a water solution which was poured into a copper cup cooled to liquid nitrogen temperature and then kept in liquid nitrogen for 10 minutes. The solution contained 1% weight PEG (Aldrich, average molecular weight: 1500 g/mole), which was dissolved in the “liquid matrix” and homogenized by an ultrasound bath for 5 minutes prior to the freezing procedure. Finally, the 20-mm-diameter target cup of a depth of 6 mm with the ice matrix was inserted into the vacuum chamber at the cryogenic target holder system cooled by a heat exchanger with cold nitrogen gas. The target temperature was controlled by a feed-back system and was kept at – 50°C for water ice and at – 100°C for the other frozen matrices.

![Deposition Yield vs. Melting Point](image)

**Figure 1.** Deposit of a 1% PEG solution for laser fluences between 2 and 10 J/cm² for a beam spot of 0.008 cm². Target temperature was -100°C except for water ice (-50°C). The squares indicate the deposit minus the yield from pure solvent.

The deposition of PEG in normal direction was monitored by a quartz crystal microbalance (QCM) with a 6-mm-diameter active silver electrode in a distance of 60 mm from the target. The accuracy of
the measurements was about 0.1 Hz corresponding to $1.29 \times 10^{15}$ amu/cm$^2$ [6,7]. Each run with the QCM was taken with a rastering laser beam to avoid hole-drilling in the ice. Usually, a deposition was carried out with 1800 pulses at a repetition rate of 2 Hz. A typical deposition rate in water ice was between 0.2 ng/cm$^2$ and 0.7 ng/cm$^2$ per pulse.

3. Results and discussion

We have deposited PEG films in the fluence range from 2 to 10 J/cm$^2$. It turned out that the deposition yield measured by a QCM was almost independent of the fluence for a beam spot of 0.008 cm$^2$. One possibility is that only a surface layer of a certain depth of the matrix contributes to the ablation, while the material from larger depth recondenses on the wall of the beam spot crater or on the material surface. We have compared the average deposition yield per pulse for four different solvents which are frequently used in MAPLE, isopropanol, acetone, toluene and water, Fig. 1. A similar run has been carried out for the frozen solvent without PEG, and the deposition of the decomposed ice was measured as well. It is seen clearly that there is no contribution from water and isopropanol ice to the deposition.

An important question in this connection is the absorption mechanism for light at 355 nm. For all matrices considered in Fig. 1, there is no (linear) absorption in the liquid except for acetone [12]. However, the absorption properties change considerably from the liquid to the ice, in particular close to the absorption edge [8,12]. However, at the fluence used in the present work nonlinear absorption occurs in all the solid matrices.

Figure 2. The deposition yield from 1%-PEG matrix as a function of the target holder temperature for a 1% PEG solution water ice matrix. Fluence 7.2 J/cm$^2$, at 355 nm; beam spot area, 0.008 cm$^2$.

Water is much less volatile than the three other liquids which all have a melting point between
178 K and 185 K. It is clear that a significant part of the evaporation is caused by laser-induced heating in addition to the low-temperature yield induced by nonlinear absorption processes. It is, therefore, of interest to measure the deposition yield as a function of the target holder temperature. Unfortunately, it was not possible to measure the temperature directly of the ice directly, but the metal holder temperature is presumably a reasonable parameter for the ice temperature.

The increase of the deposition for temperatures larger than 240 K (~ - 35°C) is significant, and could, in principle, lead to optimization of the MAPLE process at high temperatures. However, the high temperatures also lead to an increase of the water partial pressure up to the 10^-4 mbar regime, which is not always desirable.

4. Conclusions
We have studied water ice as a matrix for the production of PEG films by MAPLE at 355 nm. The deposition rate is small compared with other matrices typically used in MAPLE, but the deposition of photofragments from the matrix can be avoided. At temperatures above ~50°C of the target holder the deposition rate increases strongly, but the evaporation pressure in the MAPLE chamber also increases drastically.

Acknowledgement
This research has been supported by a Marie Curie Fellowship (Katarzyna Rodrigo) of the European Community Programme under contract number HPMT-CT-2001-00402-04.

References
[1] Chrisey DB, Piqué A, McGill RA, Horwitz JS, Ringeisen BR, Bubb DM and Wu PK 2003 Chem. Rev. 103 553.
[2] Toftmann B, Papantonakis MR, Auyeung RCY, Kim W, O’Malley SM Bubb DM, Horwitz JS, Schou J, Johansen PM and Haglund RF 2004 Thin Solid Films 453-454 177.
[3] Mercado AL, Allmond CE, Hoekstra JG and Fitz-Gerald JM 2005 Appl. Phys. A 81 591.
[4] Ringeisen BR, Callahan J, Wu PK, Piqué A, Spargo B, McGill RA, Bucaro M, Kim H, D. M. Bubb DM, Chrisey DB 2001 Langmuir 17 3472.
[5] Berry I, Sun S, Dou Y, Wucher A and Winograd N 2003 Anal. Chem. 75 5146.
[6] Rodrigo K, Toftmann B, Schou J and Pedrys R 2004 Chem. Phys. Lett. 399 368.
[7] Toftmann B, Rodrigo K, Schou J and Pedrys R 2005 Appl. Surf. Sci. 247 211.
[8] Rodrigo K, Toftmann B, Schou J and Pedrys R 2005 J. Low Temp. Phys. 139 683.
[9] Rodrigo K, Czuba P, Toftmann B, Schou J and Pedrys R 2006, Appl. Surf. Sci. 252 4824.
[10] Bubb DM, Wu PK, Horwitz JS, Callahan JH, Galicia M, Vertes A, McGill RA, Houser EJ, Ringeisen BR, Chrisey DB 2002, J. Appl. Phys. 91 2055.
[11] Kingshott P, Thissen H and Griesser HJ 2002, Biomat. 23 2043.
[12] Toftmann B 2004, Thesis (Risø National Laboratory, unpublished).