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# Structural and optical properties of phenylalanine and tyrosine thin films prepared by pulsed laser deposition

M A Hernandez-Perez<sup>1</sup>, C Garapon<sup>1</sup>, C Champeaux<sup>2</sup>, J C Orlianges<sup>2</sup>

<sup>1</sup>Laboratoire de Physico-Chimie des Matériaux Luminescents, CNRS-Université Lyon I, 10 rue André-Marie Ampère, 69622 Villeurbanne France

<sup>2</sup>Science des Procédés Céramiques et Traitement de Surface, CNRS-Université de Limoges, 123, avenue Albert Thomas, 87060 Limoges, France

garapon@pcml.univ-lyon1.fr

**Abstract.** Thin films of the amino-acids phenylalanine (Phe) and tyrosine (Tyr) were prepared by PLD with a KrF laser at fluences of some hundreds mJ/cm<sup>2</sup>. Conservation of the chemical structure and a metastable modification of the molecular interactions are evidenced by IR spectroscopy. The evolution of the refractive indices with fluence was correlated with the structure determined by X ray diffraction. Phe plume expansion imaging was achieved.

## 1. Introduction

Pulsed laser deposition (PLD) is a known method to grow inorganic thin films. Although it is still controversial, it has been shown for a few years, that conventional PLD can provide high quality thin films of organic materials too, as for example in the case of several small organic molecules [1-4] of optical or biological interest. On the contrary, matrix assisted pulsed laser evaporation (MAPLE) is considered especially attractive for large biomolecules deposition [5].

Phenylalanine (Phe) is an aromatic amino-acid, which has chirality and luminescence properties, attractive for chemical or biochemical sensor applications. We already reported the preparation of Phe films [6], with preserved chemical composition and with novel waveguiding properties. The films have the same crystalline structure as crystals, the hydrogen bonds, the origin of the molecular organization, are however stronger in the films.

The aim of this paper is to show that the modified molecular organization induced by PLD in Phe films is metastable and to estimate, by plume expansion imaging, the energy of the deposited molecules. The structural and optical properties of Phe films are compared to those of films of the amino-acid tyrosine (Tyr), which is derived from Phe (C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-CH(NH<sub>2</sub>)-COOH) by adding an OH group on the phenyl ring, which should modify the molecular interactions.

## 2. Film preparation

Films of 500 nm to some μm thickness were deposited at room temperature on SiO<sub>2</sub> substrates. A KrF laser (λ=248 nm) was used for the ablation of targets made of pressed powders. Depositions were carried out under dynamic pumping, the 10<sup>-8</sup> mbar base pressure of the high vacuum chamber increasing to 10<sup>-6</sup> to 10<sup>-5</sup> mbar during the deposition, depending on the fluence. The laser beam was

focused to a 2 mm<sup>2</sup> spot. Fluences were adjusted in the range 0.08 to 0.7 J/cm<sup>2</sup> with an Optec 4020 beam attenuator.

### 3. Structural properties of Phe and Tyr films

Chemical composition and molecular interactions of Phe and Tyr films were investigated using a Perkin-Elmer 2000 FTIR spectrometer in attenuated total reflection (ATR) configuration. Figure 1 gives the FTIR spectrum of Phe powder and, as an example, those of the same Phe film deposited at 0.08 J/cm<sup>2</sup>, registered immediately after deposition and 10 or 38 months later. These last spectra are nearly identical to that of the powder, showing that the Phe molecule is deposited without degradation nor formation of peptide bonds. However, the spectrum of the film just after deposition, although presenting the main characteristic features of the zwitterionic form of the molecule as for powder, is clearly different. It is characterized by shifts, from 1558 to 1588 cm<sup>-1</sup> and 1410 to 1403 cm<sup>-1</sup> for COO<sup>-</sup> asymmetric and symmetric stretching vibrations and from 1495 to 1515 cm<sup>-1</sup> for NH<sub>3</sub><sup>+</sup> symmetric bending and 3000 to about 2900 cm<sup>-1</sup> for NH<sub>3</sub><sup>+</sup> stretching vibrations, which were attributed to a strengthening of the hydrogen bonding in the films relative to the powder [6]. A specific molecular organization is thus induced in the film by PLD, which slowly relax to that observed in the powder, as revealed by the COO<sup>-</sup> and NH<sub>3</sub><sup>+</sup> vibrations, recovering positions similar to those of the powder in a time scale of some months or even years. At all fluences, the conservation of the molecule structure and the structural modification and relaxation were observed.

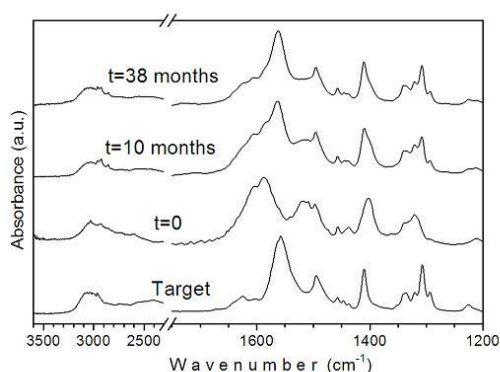


Figure 1 FTIR spectra of Phe powder and of a 0.08 J/cm<sup>2</sup> deposited film measured at different times after deposition.

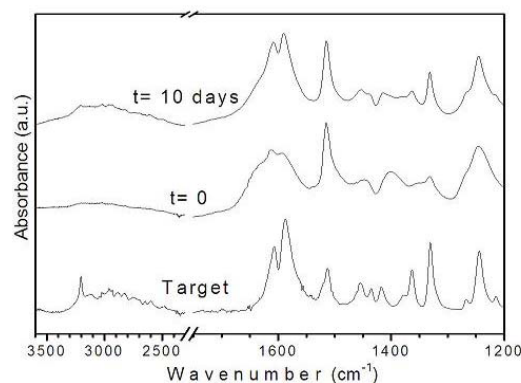


Figure 2 FTIR spectra of Tyr powder and of a 0.31 J/cm<sup>2</sup> deposited film measured at different times after deposition.

Tyr films were prepared in order to study how the phenol OH group may influence the H bonds system. Figure 2 gives the spectra of Tyr powder and of a Tyr film deposited at 0.31 J/cm<sup>2</sup>, registered immediately after deposition and ten days later. These spectra are nearly identical and are constituted of bands, which may all be assigned to tyrosine [7]. The conservation of the molecular structure is thus clearly demonstrated. A broadening of the lines involving the ring vibrations (1607, 1587, 1513 and 1331 cm<sup>-1</sup>) and those of the phenol OH group (1363 and 1244 cm<sup>-1</sup>, respectively O-H bending and C-C-O stretching) as well as the intensity decrease of the OH stretching band at 3200 cm<sup>-1</sup> show, however, that the environment of the tyrosine molecules is different in the films compared to that in the powder. These modifications are evident, when the IR spectra are recorded immediately after deposition, and then decrease at a time scale of some days. The spectra recorded after 10 days are almost identical to that of the powder. The phenol OH group clearly dominates the molecular arrangement. The same behavior, showing that Tyr is deposited without degradation in a slightly modified metastable arrangement, has been observed within the whole 0.08-0.7 J/cm<sup>2</sup> fluence range.

X ray diffraction spectra were registered using a Siemens D500 diffractometer operating in  $\theta/2\theta$  configuration. At all fluences, Phe films are crystalline with a strong preferred orientation [6]. On the contrary, Tyr films are amorphous. This may be due to the phenol OH group of Tyr, which destroys the hydrogen bonding system between  $\text{COO}^-$  and  $\text{NH}_3^+$ , which is at the origin of the double layer structure of Phe [6].

#### 4. Refractive indices of Phe and Tyr films

Refractive indices, which have not been reported yet for Phe or Tyr crystals, were measured by m-lines spectroscopy using a polarized He-Ne laser beam launched into the film by means of a high refractive index prism, at two wavelengths, 543.5 and 632.8 nm, for TE (transverse electric) and TM (transverse magnetic) modes. For all films, the thickness is the same for both polarizations and wavelengths, showing the validity of the step index profile assumption used for the calculation.

The refractive indices of Phe films do not depend on fluence [6]. They show a strong anisotropy, in agreement with the strong crystalline orientation. The mean refractive index at 543.5 nm, for films deposited between 0.08 and  $0.7 \text{ J/cm}^2$ , are  $n_{\text{TE}} = 1.619 \pm 0.001$  and  $n_{\text{TM}} = 1.606 \pm 0.002$ .

Figure 3 gives the refractive indices and thickness of tyrosine films as a function of fluence. Thickness is normalized relative to the deposition time and thus expressed as deposition rate. The refractive index increases with increasing fluence to reach an almost constant value above  $0.47 \text{ J/cm}^2$ , indicative of a densification effect of the fluence on the amorphous Tyr phase. The indices are the same for TE and TM polarizations, being for example  $n_{\text{TE}} = 1.644 \pm 0.001$  and  $n_{\text{TM}} = 1.643 \pm 0.002$  at 543.5 nm for a film deposited at  $0.31 \text{ J/cm}^2$ , which shows that the films are isotropic, in agreement with their amorphous structure.

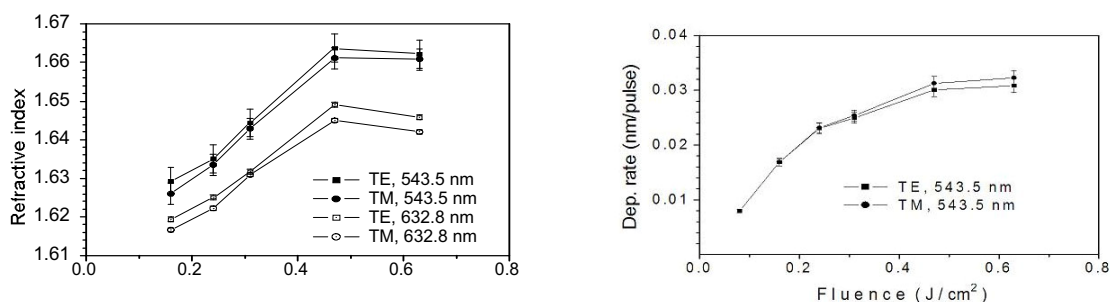


Figure 3 Refractive index (left) and deposition rate (right) of Tyr films versus fluence

Tyr deposition rate increases with increasing fluence, reaching saturation at high fluence. The same evolution was observed for Phe. The deposition rates are about 5 times lower for Tyr than for Phe [6], which may be due to a lower absorption. On the contrary the 248 nm wavelength of the KrF laser exactly matches a Phe absorption peak.

#### 5. Phe plume expansion imaging

Phe plume has been imaged, by recording with an ICCD camera the emitted light without external excitation. We used the lowest fluence for which a signal could be detected,  $0.7 \text{ J/cm}^2$ . For this fluence, the molecule is deposited without degradation.

Figure 4 a gives examples of the image of the plume registered as a function of time between 0 and 1500 ns after the end of the laser pulse. The positions of the plume leading edges in the axial (Z) and radial (R) directions and of the mass center, determined as the brightest point of the plume, are given versus time in Figure 4 b. Two steps may be detected: 1D expansion until 400 ns and then 3D expansion, when the Z/R ratio levels to a constant value. From these curves, the axial and radial expansion velocities are found equal to 19 and 10 km/s, respectively. These high velocities may probably explain why, in the films, a metastable molecular arrangement, different from that in equilibrium grown crystals could be induced.

For organic molecules, plume imaging in the experimental conditions corresponding to deposition has not been reported yet to our knowledge. The comparison of our results with literature is thus restricted to data corresponding to the conditions of a MALDI experiment. For an ablation fluence of  $0.05 \text{ J/cm}^2$  and from plume imaging by laser induced fluorescence, axial and radial velocities of 1.5 and 0.5 km/s were measured for the matrix molecules of 3-hydroxy-picolinic acid, which have similar molecular weight as Phe ( $M=139$  and  $165 \text{ g/mol}$  respectively) [8]. Thus more than one order of magnitude, lower velocities may be explained by the much lower fluence and by the fact that detected species were different. We detect at short time excited molecules, whereas in the MALDI experiment the species were detected at longer time and were molecules excited by a second laser in the plume.

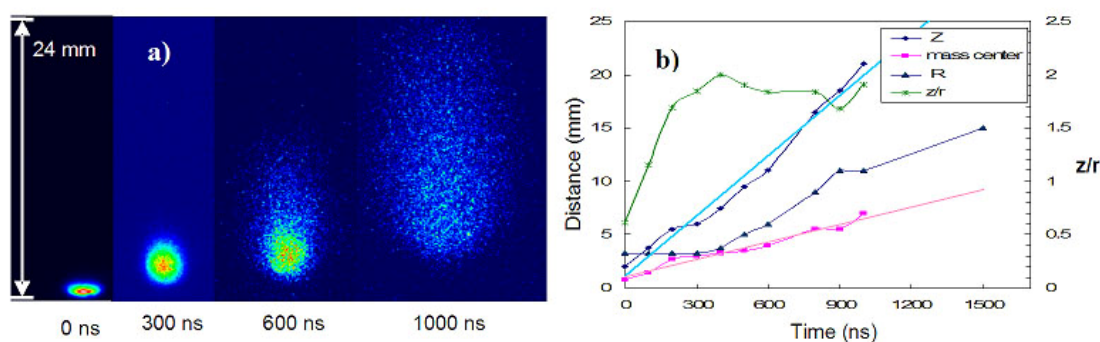


Figure 4 Images of Phe plume registered by ICCD and axial Z and radial R leading edges and mass center positions as a function of time after the KrF laser pulse (Fluence  $0.7 \text{ J/cm}^2$ )

## 6. Conclusion

Phe and Tyr films were prepared by PLD with a KrF laser at fluences between  $0.08$  and  $0.7 \text{ J/cm}^2$ , without degradation of the chemical structure. Their refractive indices were measured for the first time. They are anisotropic and independent of fluence for the crystalline and highly oriented Phe films. They are isotropic and increasing with fluence for the amorphous Tyr films, showing densification by fluence. PLD induces, at molecular level, metastable arrangements. For Phe, the hydrogen bonding system, at the origin of the crystalline structure, is stronger in PLD films and relax very slowly towards that of crystal. This may be due to the high velocities of the ablated molecules, which have been estimated from Phe plume expansion imaging. The amorphous Tyr films, for which the additional OH group modifies molecular interactions, show a more rapid relaxation.

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