

# **Pulsed laser deposition of organic materials**

PhD theses

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## **I. Introduction**

Since the first laser had been demonstrated about a half century ago, lasers became a standard and widely employed tool not in the research laboratories, but also in many fields of technology and engineering. Several techniques were developed on this field; one of them was the materials and tissue engineering by pulsed lasers.

Over the past few years, the pulsed laser deposition (PLD) technique has emerged as one of the simplest and most versatile methods for the deposition of thin films of wide variety of materials. Combined with a stoichiometry transfer between target and substrate this allows depositing many kinds of different materials. In last few years, many investigation were have been performed in order to produce organic and biomaterial thin films by PLD.

## **II. Scientific background and aims**

Shortly after the discovery of the laser, researchers began irradiating almost every conceivable target material and phase for novel basic physical and chemical study in addition to new applications. Pulsed-laser deposition (PLD) is a highly flexible thin-film growth technique which has been successfully applied to a wide range of materials [1]. In the laser ablation process, high-power laser pulses are focused onto the surface of a bulk target typically at an angle of incidence of  $45^\circ$  with respect to its perpendicular direction. The ablation of the target produces a visible plasma (commonly known as "plume") that expands from the target.

The created a plume explosively expands towards the deposition substrate, creating a thin layer of material in 10-50 ns. One of the advantages of PLD is that the process can be performed at any pressure ranging from ultra high vacuum to high pressures (typically up to 10 mbar) and that any kind of atmosphere either inert or reactive can be used. Deposit properties obtained by PLD can be controlled by choosing different irradiation parameters such as laser wavelength, fluence, number of pulses, and pulse duration. The characteristics of the deposits also depend on the nature of the target, the temperature of the substrate and the background pressure or gas in the deposition chamber. One of the main drawbacks of the PLD technique addressed in the literature is the generation of particulates of sizes up to a few  $\mu\text{m}$  that are deposited on the growing film, leading to rough and thus low quality films. One way to overcome this problem is through the use of very dense or single crystalline materials as targets, together with selection of appropriate experimental conditions.

Even at low fluences, some polymers and biomaterials are extremely photosensitive. With an improved understanding of the laser-material interaction and the discovery of new laser-material combinations, lasers have proven to be powerful tools in the novel processing of polymer and biomaterial films.

The aim of my PhD theses was to create organic thin films with the chemical composition close to the original materials using pulsed laser deposition technique. The aim was the optimalization of the deposited parameters like laser fluence, number of pulses, target-substrate distance, etc. The purpose of my studies was to deposit human tooth thin films onto titanium surface as a optional function as a medical application. My aim was to create pepsin thin layers with the remaining biological function; a biopolymer, poly-hydroxy-butyrate (PHB) thin film deposition; femtosecond PLD of cell growth promoting thin layers. My last goal was to investigating the size and the properties of the deposited particles of poly-metyl-metacrylate (PMMA).

### **III. Results**

The main theme of my theses was the pulsed laser deposition of biological and biocompatible materials. During the present study I was working on different experiments with the aim of the deposition of thin films with proper chemical compositions and biological functions.

#### **1. Pulsed laser deposition of human tooth onto titanium surface**

In the recent years, the applications of implants are very common on many field of the medicine. The basic requirement from these is the biocompatibility to fit into to the living organism. According to the results of the tooth implants, it is very common that the human body does not accept the metal surface, (and the osteo-integration is not occurring) causing the rejection of the implants. I wanted to prove with my experiments that it is possible to create bio-, human tooth thin films by pulsed laser deposition onto titanium disks.

**1. a** It was shown that it is possible to make thin layers with similar chemical composition to the original tooth material using PLD method. The FTIR measurements proved that during the process of the deposition the amount of  $\text{OH}^-$ ,  $\text{H}_2\text{O}$  and the carbonate is decreasing which means, that because of the raise of the temperature - caused by the laser radiation –  $\text{H}_2\text{O}$  and  $\text{CO}_2$  will release from the material of the tooth. [T1].

**1. b** The  $\text{CO}_3$  content can be increased with post annealing of the films at  $550\text{ }^\circ\text{C}$  shown that the pressing pressure from 150 to 450 MPa led to the change of the deposition rate and the roughness of the deposited layers. With post annealing the resistance of the films could be improved against the mechanical effects [T1].

## **2. Pepsin thin films by PLD technique**

During the PLD of biological materials the experimental parameters are very important, because the molecules have thermal effects and the formations can be damage the biological functions and catalytic ability of the layers. Successful thin film deposition only can be done if we can prove that the enzymatic properties of the layers are remaining.

**2. a** I established by the infrared spectral measurements that under the used fluences the spectra of the deposited films at 0,5 and 1,3 J/cm<sup>2</sup> fluences are nearly identical over the entire studied spectral range, which means that the chemical composition of the samples is basically the same. The layers were investigated by optical and atomic force microscopy (AFM).

**2. b** It was shown that that the layers were contiguous, and the surfaces of the thin films appeared granular. To prove the biological activity, I used a glass chamber isolated from its environment filled with vapour of 0,4% HCl solution and the temperature was constant 37 °C corresponding to the temperature of the human stomach. Enzyme activity test proved that the majority of transferred enzyme retains its biological function in 0,38–1,22 J/cm<sup>2</sup> range - but not on 2,43 J/cm<sup>2</sup> - supporting the results of FTIR measurements. Probably the layers deposited on higher fluences loosing their digestive properties, due to the strong damage effect of the laser irradiation [T2].

## **3. Pulsed laser deposition of biodegradable poly-hydroxy-butyrate**

It is a new challenge for the material science to deal with the connection and interaction between living tissues and different materials. The main challenge is

to create and process biocompatible materials with the aim to promote the successful function of device during the application. I was using poly-hydroxybutyrate as a target material to deposit thin layers by PLD technique.

- 3.a** It was demonstrated, that stoichiometric PHB layer can be produced by pulse laser deposition.
- 3.b** I established the range of the optimal fluences to make these thin films. Infrared spectroscopic measurements proved that the important functional groups of the transferred biopolymer can be preserved during the PLD procedure using appropriate ( $0.12 \text{ J/cm}^2$ ) fluence [T3].
- 3.c** On the basis of the ellipsometric analysis the wavelength dependence of the refractive index, the extinction coefficient and also the absorption coefficient of the deposited PHB layer were determined. These are important information about the PHB because these parameters are not found in the scientific literature before [T3].

#### **4. Pulsed laser deposition of cell growth promoting thin layers**

- 4.a** Thin films of cell growth-promoting substances were deposited using PLD. In this study I have shown that various biomaterials transferred by PLD methods onto silicon plates successfully guide the adhesion and growth of different cell types [T4].
- 4.b** The deposited materials were Na-alginate, fibronectin, endothelial cell growth supplement and collagen embedded in starch matrix. It was shown that any kind of structure can be deposited from the target materials, using a mask. The results are suggesting that PLD method is suitable to build an architecture of substrates

which supports and directs the growth of cells. The guided growth may enable the cells to induce directed and rapid repair of injured tissues [T4].

## **5. Characterization of particle ejection in the UV nanosecond ablation of PMMA**

With the aim of creating nano particles of the poly-methyl-metacrylate, I was using a standard pulsed laser deposition setup to make the deposits. I was investigating the size and the properties of the deposited particles.

**5.a** I was investigated that what kind of experimental parameters causing the smallest ejected particles from the polymer target. In the experiments I was using three different type of excimer laser with wavelengths of 193, 248 and 308 nm to irradiate the target materials. The targets were made of different molecular weight of PMMAs and the applied fluences were changed during the depositions.

**5.b** I established that the smallest particles were ejected from the PMMA using ArF excimer laser beam at  $0,1 \text{ J/cm}^2$  fluence [T5].

## **IV. References**

The thesis is based on the following articles appeared in referred international journals:

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