# Laser methods for deposition of Teflon thin films and modification of Teflon's adhesion properties

PhD thesis

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# I. Introduction

Nowadays, more and more people are affected by allergic-type diseases. Its reason is not only the wider knowledge of the symptoms but the cumulative environmental harms, the unnatural materials which we meet and touch day by day contributes to the raising of the number of affections. The frequent contact with allergenic materials results in more intense allergic reactions, moreover, according to the present medicine the allergenic diseases are not curable, the treatment tends to the easement of symptoms. That's why the most important role of the allergic patients is the avoidance of contact with allergenics, i.e. the prevention.

Allergic symptoms induced by some metals are very frequent, which could be provoked by metal objects often contacting the skin. Such are the articles for everyday personal use, e.g. backboard of watch, spectacle-frame, different jewels or metal medical implants. These are mostly alloys contain nickel – the most frequent metal allergen. Moreover, there are patients are sensitive to gold, silver, and even titanium, which is considered a biologically inactive material! For these patients a solution could be a protective layer preventing the contact between the given metal object and skin surface, and thus the reaching by allergens of the organism. The suitable protective-insulator layer has to be biologically inert, chemically resistant, impenetrable for metal ions and stick properly to bearing surface.

In the course of my work I have examined the possibility of formation of such protective layer, among others. The Teflon (politetrafluoroethylene, PTFE) could be a right choice due to several excellent qualities: it is chemically extremely stable material; it is also characterized by high chemical resistance and it is biologically inactive, which allow medical and biological application. The well-known low adhesion of the Teflon can be a difficulty for applications when for example sticking, fixing or cell adhesion to implants is needed. For this reason the possibility of adhesion enhancement was also studied.

# II. Scientific background and aims

One method suitable for production of Teflon thin layers is the Pulsed Laser Deposition (PLD). In the procedure a target placed in a vacuum chamber is irradiated with a high fluence pulsed laser beam. As a consequence of the laser irradiation the ablation takes place: a material cloud (plume) is emitted perpendicularly from the irradiated surface. The ejected material can be collected onto a substrate facing the target, forming a thin layer. The advantages of the method are the compact film structure caused by the energetic particles of the plume, the thickness of the film can be precisely controlled with the number of laser pulses and whit appropriate experimental parameters stoichiometric deposition can be achieved.

In the last years several studies dealt with pulsed laser deposition of Teflon thin films using ultra violet pulsed lasers. Since the molecular structure is decomposed in a non-controllable way by the high intensity laser irradiation, the UV photo-ablation of organic materials is considered more suitable for material removal than thin film deposition. Nevertheless, spectroscopic investigations proved that under appropriate parameters the PLD technology can be used for stoichiometric Teflon film deposition [1-2]. The composition and structure of the deposits also depends on the substrate temperature applied during the process [3-5].

My aim was the determination of experimental parameters suitable for depositing thin films that adhere to the metal substrates and can prevent the pass through of metal ions in order to isolate the human body from the allergenic objects.

The best known property of the Teflon is its adhesive behavior. Due to its low surface energy it is non-wettable by any liquid and can not be directly sticked. This low adhesion can be a problem when sticking or painting of the Teflon is needed.

The laser surface treatment can influence the surface adhesion of the PTFE in two ways. When the aim is the modification of surface topography without any change in other physical or chemical properties the use of femtosecond or deep-UV ($\lambda$<170 nm) excimer lasers is favourable [6-9].

The other method is directed to the change of surface chemical properties of the sample. When a PTFE foil is irradiated with an ArF excimer laser beam ($\lambda$=193 nm) photoinduced reaction can take place between the molecules of Teflon and another material placed on its surface, leading to chemical changes. Chatib and co-workers demonstrated this photoreaction even in the presence of the air moisture [10]: as a consequence of 300 mJ/cm$^2$ irradiation OH groups were built into the polymer chain accompanied with HF release. Murahara, Okoshi and Toyada used different boron compounds [11-13]. The oleophilic properties of the PTFE could be increased with laser irradiation of samples immersed in 5-40 Torr pressure trimethylboron ($B(CH_3)_3$) gas [12] caused by linking of $CH_3$ groups to the molecules of the surface. When the excimer laser treatment was performed trough a thin layer of sodium-borohydrid ($NaBH_4$)-methylene solution the fluorine atoms of the surface were exchanged by $CH_3$ and OH groups. In the above mentioned experiments the sticking properties of the modified surfaces were studied. It was found that the adhesion strength of the epoxy-resin sticking significantly increased. Niino and Yabe used compounds containing amino groups as reactive material, the wetting angle measured with water was found to decrease from 130° to 30° [14].

Károly Révész and colleagues used triethyl-amine and 1,2 diaminoethane for photochemical modification [15-16]. It was shown that whit these reagents the method is highly effective at even very low fluences (<1mJ/cm$^2$) as compared to the previously mentioned cases where 10-300 mJ/cm$^2$ fluences were needed. They also demonstrated that as an effect of 0.4 mJ/cm$^2$ treatment the wetting angle measured for water rapidly decreased from 94° to less than 50°, while the adhesion strength of sticking increased from 0.03 MPa to 5-6 MPa after applying 1000 laser pulses.

When using the last mentioned materials amine groups replaced the fluorine atoms of the Teflon chain in the course of photoinduced reaction. My aim was to investigate whether the efficiency of the process can be increased by using molecules containing more amine groups, i.e. how the wetting angle and adhesion strength changes when using similar irradiating parameters (fluence, laser pulse number).

# III. RESULTS

## 1. The influence of the particulate size on pulsed laser deposition of Teflon

As a first step the process of the layer growth was studied. During the laser ablation the removed material leaves the Teflon surface in two steps: a plasma state material cloud is followed separated in time by micron sized particles. Since the majority of the ablated material is consisted by these micron sized particles the depositing layer is mostly built up of these. Since the size (size distribution) of the removed particles depend on the ablating fluence, this also influences the structure of the growing layer. For this reason a series of experiments were performed when the particles removed by ablation were collected on a silica substrate under circumstances corresponding to the real deposition. Based on the obtained size distribution and the particle diameter-volume relationship the formation of thin film was simulated using a Maple program. The program counted the total volume of the deposited particulates and from this the average thickness of the film was calculated.

1.a. It was shown that the increase of the fluence the number of pulses required to obtain contiguous layer decreased while the minimum thickness of the contiguous layer increased. [T1]

1.b. The reason of this is the increasing average particle size and the particulate density when increasing the laser fluence. The thicknesses given by the simulations were in good agreement with the experimental results obtained on deposited and post-annealed layers. [T1].

## 2. Deposition of biologically inert Teflon protective layers on surface of allergenic metals by pulsed laser deposition

The aim of the experiments to deposit on allergenic metal surfaces (14 carat gold, silver, titanium) Teflon thin films that can prevent the contact between human body and the allergenic object. The system used for the deposition was designed and built. The optimum depositing parameters were determined on the basis of the measurements performed on thin layers produced on glass and KBr substrates. Then films were deposited on the above mentioned metal surfaces under optimum conditions.

2.a. Sponge like structured thin films were produced at the optimized parameters. It was shown that their structures can be modified from micrometer sized grains to 600 µm crystalline plates with post annealing depending on the applied temperature and cooling rate. Production of ringed structure Teflon films was published in the literature for the first time. Compact thin films can be formed at 360-500°C post annealing which also results in decrease of the film thickness by 50%. [T2, T3].

2.b. FTIR measurements proved that at 250°C substrate temperature and 1.7-9.0 $J/cm^2$ fluence the chemical composition of the films deposited on the KBr substrates corresponds to the started material, as also confirmed by the XPS spectroscopy. The 360°C post annealing preserved the chemical composition of the deposits, while at 500°C only slight modification in polymer chain was caused (traces of –CF– and –$CF_3$– were observed). [T2]

2.c. It vas proved that the layers deposited on 14 carat gold, silver and titanium substrates became contiguous, compact and nearly transparent as a consequence of the 360°C post annealing. At this temperature (within the studied range) the best adherence to the substrate was obtained. The chemical isolation ability of such films was studied for the first time in literature. The films having few micrometer thickness were able to prevent the pass through of different ions for several hours. [T4]

On the basis of these can be affirmed that the Teflon layers produced by pulsed laser deposition and post annealed at appropriate temperature can be used as protective layers.

## 3. Change of adhesive properties of Teflon foils with UV laser irradiation

Due to its well known adhesive properties the Teflon is not wettable and its sticking is also difficult. This problem can be solved by surface chemical modifications. This was realized by photoinduced reaction between the Teflon and photoreagents in presence of UV laser light.

Three types of liquid amin photoreagents were used: aminoethanol, 1,2 diaminoethane and triethylene-tetramine. The Teflon foils were irradiated with the same laser parameters for all the reagents.

3.a. The wetting angle of distilled water was measured as the function of the laser fluence on Teflon foils treated in presence of different photoreagent materials. Without the use of photoreagent the laser irradiation did not change the wetting angle, while when using the amine compounds the angle decreased its half or even third part. The most significant change caused by the triethylene-tetramine. [T5]

3.b. The influence of the treatment on the adhesion strength was measured by sticking Teflon foils treated similarly on both sides. It was proven that the adhesion strength significantly increased for all the three reagents when increasing the laser fluence in the 0–1 $mJ/cm^2$ range. The most effective was the treatment in presence of triethylene-tetramine. Atomic force microscopic investigations showed, that the change in the surface roughness was insignificant, this means that the increase of adhesion strength can be attributed to the chemical changes on the surfaces of the Teflon foil. [T5]

3.c. Finally a demonstrative experiment was performed, where a Teflon foil treated with triethylene-tetramine was immersed in a cell culture. After one week incubation time the foil was washed, dehydrated and fixed. Atomic force microscopic measurements indicated that the cells adhered to the treated surfaces, while the untreated area was completely free of cells. This is an important result from point of view medical applications. [T5]

## IV. References

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


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