# Interaction between ultrashort laser pulses and metal or semimetal target materials

*PhD thesis book*

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# 1. Introduction

The development of the ultrashort laser pulses resulted in the important research field of interactions between ultrashort laser pulses and matter. The unique properties of the short laser pulses like the instant energy release, the extreme high laser intensities opened a wide possibility in their applications as surface micromachining, pulsed laser ablation, pulsed laser deposition, generation of nanoparticles, or in plasma and atomic physics. Nowadays the ultrashort laser pulses are routinely used in research laboratories, their application in the industrial sector is gradually increasing, although these laser sources were developed only two decades ago.

When the laser pulse irradiates the surface of the target, matter is ejected and forms a cloud above the surface. The properties of the ablated plume rather differ from the ns or ps laser pulse generated plume, because the fs pulse is not interacting with the formed plume due to its short term. The energy of the laser pulse is absorbed in a thin surface layer of the target, and heats it to a high temperature without important heat conduction into the bulk material, which makes the fs laser pulse a promising light source for pulsed laser ablation (PLA). In the case of ns pulses during the micromachining of metal targets it was observed that the heat diffusion length is larger than a μm which prevents the sub- micrometer surface treatments. By applying fs laser pulses the precision micromachining of metals, semimetals, semiconductors, polymers, dielectrics, transparent and opaque materials can be achieved. On the contrary in the case of ns laser pulses different target materials require variable laser sources. On the other hand the heat diffusion lengths are much shorter for fs pulses than for ns, therefore the heat affected zone are significantly reduced. These properties induced several new possibilities to apply fs laser systems in biology, in eye-surgery, or in diagnostics, cleaning, and conservation of fine-art objects.

The fs laser pulses are used in pulsed laser deposition (PLD) method as well. The ultrashort laser pulse generated ablation plumes contain highly energetic atoms and ions. These particles can play an important role in the deposition of special layers, e. g. for tribological applications. In addition to that, the PLA technique is employed to produce nanoparticles due to the simplicity and efficiency of the method. The usage of the fs laser pulses opened up a new perspective to prepare nanoparticles without aggregation effects. Furthermore, due to the short time period of the laser pulse, the interaction between the fs laser pulses and the plume could be neglected. Finally it has to be mentioned that narrow size distribution of the particles can be achieved.

In order to control the ablation procedure, the micromachining of the surfaces, the properties of the deposited layers and nanoparticles the subsequence processes following the laser irradiation has to be well known. Though the fs laser pulses are applied in a wide-range of research fields the researchers were facing several difficulties to describe theoretically the interactions between the laser pulse and the matter. The processes are rather complex, therefore a theory, which is able to describe the interactions and their consequences for any kind of material uniformly are still lacking. On the contrary, numerous models are developed in order to describe and to predict these interactions for special target materials, and size range with adequate precision (e. g. two-temperature thermal diffusion model, molecular dynamics simulations). The evolution of the models, their verification, and the explanation of the processes are based on experimental observations, experiences.

## 2. Goals

The aim of my thesis work was to investigate the interactions of the ultrashort laser pulse with metal and semimetal targets from two main aspects. My purpose was to study the effect of the irradiating laser intensity on the ablated plume, the deposited matter (layers or nanoparticles), and the ablated crater on the target surface.

Furthermore by applying double, fs laser pulses I planned to examine the change of the laser ablated matter induced by the time-delayed, second laser pulse. Therefore, I investigated the impact of the modified ablated plume on the characteristics of the deposited material, as thin films or nanoparticles.

## 3. Experimental methods

In-situ and ex-situ methods were used to characterize the processes induced by the irradiation of the ultrashort laser pulses on the target material.

Femtosecond laser pulses of a four stage amplifier colliding pulse mode locked dye laser (LOA, Laboratoire d'Optique Appliquée, Palaiseau, France) irradiated and ablated the surface of a copper target. The target was placed into a home-made vacuum chamber, where the residual pressure was $\sim 10^{-4}$ Pa. The evolution of the fs laser pulse generated plume was studied in-situ by a frequency doubled, delayed, second laser pulse. This delayed pulse reflected on the target surface after the ablation with the first pulse, and the detection of its intensity change allowed to gain information about the processes on the surface.

I studied the properties of the surface of the copper disk irradiated by single, and multiple ultrashort laser pulses. The surface structures were observed by field emission scanning electron microscope (FESEM, SZTE TTIK and LOA). The ablated craters induced by multiple laser pulses were investigated with surface profilometer (DEKTAK 8 profilometer, SZTE Optikai és Kvantumelektronikai Tanszék), which provided information about the shape, the depth and the volume of the craters.

The ablated plume was deposited to the surface of a Si substrate, and the deposited nanoparticles were analyzed. The dependence of their properties on the irradiating laser pulse intensity in the range of $4{,}4 \cdot 10^{12}$-$4{,}4 \cdot 10^{13}$ W/cm$^2$, and on the time-delay between the double laser pulses were studied. From images taken by a field emission scanning electron microscope (FESEM, SZTE TTIK) and an atomic force microscope (SZTE, Institute of Optics and Quantum Electronics) the structure, shape, and size-distribution of the nanoparticles were determined. The double laser pulses for the experiments are generated in a Michelson interferometer.

A glassy–carbon target was ablated by ultrashort laser pulses from a Ti:sapphire oscillator-amplifier laser system and a KrF excimer-dye laser system (FORTH Institute of Electronic Structure & Laser, Heraklion, Greece). The experiments were performed in a vacuum chamber with residual pressure of ~$10^{-4}$ Pa. The ablated plume induced by the Ti:sapphire laser system was studied by Laser Induced Breakdown Spectroscopy (LIBS, FORTH Institute of Electronic Structure & Laser, Heraklion, Greece) method. The ablated surface was investigated electron microscope (FESEM, SZTE TTIK and LOA).

The ablated plume induced by pulses from Ti:sapphire laser and KrF excimer-dye laser system was deposited on a Si substrate, and diamond-like carbon (DLC) layer formed. I investigated the optical, structural, morphological properties of the DLC layers depending on the time delay between the double laser pulses, or depending on the imaging of the laser beam into the target surface (the irradiated area was changed). The optical parameters and thickness of the layers were determined from measurements by spectroscopic ellipsometry (Woollam, M2000-F ellipsometer, SZTE Department of Optics and Quantum Electronics). The structure of the thin films was analyzed by Raman-spectrometry (University of Uppsala, Renishaw micro-Raman spectrometer). As previously, the double laser pulses were produced in a Michelson interferometer.

# 4. Results

The results from my thesis work:

1. The time-resolved evolution of the ablated plume induced by fs laser pulses on copper target can be investigated by a delayed, frequency doubled laser pulse. The components of the plume are emitted from the target surface or formed above the target at different times. The time and space of the formation of the components can be determined by this technique. I experimentally demonstrated by this in-situ method that the nanoparticles are ejected directly from the target surface, and they did not form in the dense ablated plume above the surface. By analysing the deposited material on the Si substrate it was determined that the nanoparticles arrived to the Si in liquid phase [2].

2. I observed that by irradiating the copper target surface with laser beam under certain incident angle two ablation ranges can be defined from the microstructure of the target surface. I represented that by ablating the target surface with laser beam, which has not homogeneous intensity distribution, the ablation rate, which is calculated from the depth of the crater is not able to provide relevant information about the different ablation processes.

   On the contrary, the ablation processes can be characterized by determining the volumetric ablation rate as a function of the applied laser fluence. I observed that the ablation rate depends on the full number of laser pulses, which formed the ablate crater, and the efficiency of the ablation is reduced by increasing the number of laser pulses [3].

3. I have investigated the effect of the ablating ultrashort laser pulse intensity on the size-distribution of the nanoparticles ablated from a copper target. I studied the effect on the average diameter and general structural properties, as well. I proved with the properties of the nanoparticles that by applying double laser pulses the energy coupling into the target material can be controlled by changing the time-delay between the laser pulses. Therefore the size-distribution and average diameter of the nanoparticles can be effectively modified [2].

4. I studied the ablated plume formed on a glassy-carbon target material with a laser-induced background spectroscopic method (in-situ). I observed that by modifying the spot size of

the laser beam on the target surface there exists an imaging condition (different from the focus) where the population of ionic and atomic particles in the plume is maximal. I have shown that by changing the time delay between the double, ultrashort laser pulses the population of the ionic, and excited atomic particles can be modified.

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5. I applied different laser pulses (KrF excimer-dye laser system, λ=248 nm, and Ti:sappire laser oscillator, λ=800 nm) in order to ablate a glassy-carbon target. The ablated plume was deposited into a Si subsrate and the properties of the formed layer were characterized. I studied the optical, and structural properties of the layers as a function of the image condition of the laser beam, and the time-delay between the pulses at double pulse experiments. I have shown that by choosing the right laser, imaging (focusing) conditions the properties of the deposited layer, as the thickness or optical band gap can be controlled. I proved that the deposition rate has a maximum at an off focus position. I proved that the effects of the double laser pulses can be investigated through the optical and structural characteristics of the layers. [1].

## 5. Publications

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[2] Olivier Kim-Hak, Jean Lorenzzi, Nikoletta Jegenyes, Gabriel Ferro, Davy Carole, Patrick Chaudouët, Olivier Dezellus, Didier Chaussende, Jean-Claude Viala and Christian Brylinski, „Further Evidence of Nitrogen Induced Stabilization of 3C-SiC Polytype during Growth from a Si-Ge Liquid Phase”, Materials Science Forum 645-648, 163-166 (2010)

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[5] J. W. Sun, G. Zoulis, J. Lorenzzi, N. Jegenyes, S. Juillaguet, H. Peyre1, V. Souliere, G. Ferro, F. Milesi, and J. Camassel, „LTPL investigation of N-Ga and N-Al donor-acceptor pair spectra in 3C-SiC layers grown by VLS on 6H-SiC substrates", Materials Science Forum Vols. 645-648, pp 415-418 (2010)

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[10] M. Beshkova, J. Lorenzzi, N. Jegenyes, R. Vasiliaskas, J. Birch, M.Syväjärvi, G. Ferro, R. Yakimova, „Sublimation epitaxy of 3C-SiC-growth and characterization", Proceedings of International workshop on Advanced Semiconductor Materials and Devices for Power Electronic Applications (WASMPE'09) May 6th-7th, 2009 – Catania.

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