I. PRELIMINARIES AND SCOPE

Material removal from sample surface irradiated by laser pulses is called pulsed laser ablation (PLA), or, shortly, ablation. Right after the discovery of lasers in the 1960's, laser ablation was also discovered, but it came into prominence later in the 80's, when polymer ablation was first detected. By now, the literature on the ablation of metals, dielectrics and semiconductors is alike widespread. Different, thermal and non-thermal models are used for description of ablation, which are supposed to take into account the laser pulse and materials parameters and the possible interactions of those as much as possible. From technological point of view, ablation became also quite important. This is the process which corneal surgery and pulsed laser deposition (PLD) are based on, and also nanoparticles can be produced by ablation.

Nanoparticles, i.e. particles of diameter in the nanometer range, are extensively investigated recently. They also possess direct industrial applications, like for example in cosmetic industry, in waste water treatment, drug delivery experiments referring cancer treatment.

Magnetic, mechanic, electric, catalytic properties of nanoparticles are size-dependent, and may differ significantly from those of the corresponding bulk material. Thus it is essential in nanoparticle production that size distribution, chemical composition and phase of the nanoparticles should be controllable, and preferably small nanoparticles with narrow size distribution shoul be prepared.

The subject of my dissertation is ArF laser ablation of graphite. Proper understanding of the details of this process would contribute to the perfect control of the ablation based processes like carbon film or nanoparticle production by properly chosen parameters.

The objects of my doctoral work were the following:

1. Measurement of the amount of material evaporated by a laser pulse from the HOPG surface as a function of fluence. Determination of the ablation threshold fluence and the effective absorption coefficient of graphite for 193 nm wavelength by fitting a curve on the experimental data.

2. Investigation of the shockwaves emerging above the sample surface during HOPG ablation and determination of the shockwave velocity as a function of time and fluence by fast photography. Measuring the time necessary for shockwave generation. Detection of shockwaves generated by laser pulses of fluences below the ablation threshold. Detection of the material leaving the surface.

3. Approximate temperature calculation, fast photographic experiment and transmission electron microscopic imaging for answering the question whether the grafite melts or not as a consequence of ArF laser irradiation.

4. Investigation of the size distribution of nanoparticles generated by graphite ablation in nitrogen atmosphere as a function of fluence, laser repetition rate and ablated spot size. Analysis of the nanoparticles by Röntgen diffraction, Raman spectroscopy and Röntgen photoelectron spectroscopy.

5. Determination the reason of and the amount of desorbed material needed for shockwave generation. Finding connection between the quick material desorption generating the shockwave and the nanoparticle production at fluences below ablation threshold. Demonstration of the non-thermal character of quick desorption.

II. APPLIED METHODS

ZYH and ZYB grade pyrolitic graphite of Advanced Ceramics was used as ablation target. The ablation was induced by properly imaged pulses of Lambda Pysik ArF excimer lasers.

Fast photography was applied for imaging the shockwave emerging in the early phase of ablation and detection of the ablation plume. The cornerstone of this method is usage of ~1 ns long exposing dye laser pulses in an imaging system consisting of a microscope objective and a commercial video camera.

Size distribution of nanoparticles condensing in the ablation plume was taken by the SMPS 3936 system of TSI Corporation and the corresponding TSI software. The main part of this equipment is the differential mobility analyser, in which the nanoparticles are drifted by a laminar nitrogen flow between two concentric metal cylinders. Due to the bias between the cylinders only the charged nanoparticles falling in a narrow mobility size range reach the output of the device and next the condensation particle counter.

The temperature increment of the graphite was estimated by a program solving the heat equation by the method of finite differences.

The irradiated graphite surface was investigated by transmission electron microcopy, while Raman spectroscopy, Röntgen photoelectron spectroscopy and Röntgen diffraction was used for characterisation the nanoparticles deposited on a silica plate.

I was in the employment of the University of Szeged as a PhD student and next of the Department of General Physics and Laser Spectroscopy of University of Pécs during my doctoral work. Experiments were carried out in the Department of Optics and Quantum Electronics of University of Szeged and in the Ångström Laboratory of the University of Uppsala.

III. NEW SCIENTIFIC RESULTS

1. Measuring the depth of the ablation holes produced at different fluences, the ablation curve of HOPG was taken. A logarithmic function describing thermal ablation above the threshold fluence, where the absorption of the plume is not negligible, was fitted to the measured data, and thus the threshold fluence and the effective absorption coefficient of HOPG at 193 nm was determined. The ablation threshold was found to be $\Phi_{th}=(1,2\pm0,2)$ J/cm^2, while the effective absorption coefficient is $\alpha_{eff}=(1,5\pm0,3)\cdot 10^5$ 1/cm. [1]

2. The velocity of the shockwave emerging in the air above the ablated surface was measured as a function of time and fluence by fast photography. It was claimed that, at 10 ns after the incidence of the laser pulse maximum, the shockwave is already detectable. It was concluded that if the laser fluence is above the ablation threshold, then a theoretical function describing hemispherical shockwaves can be fitted to the measured data, assuming that the energy generating the shockwave is proportional to the laser energy. Shockwaves could be detected even at $\Phi=0,3$ J/cm^2 that is well below the ablation threshold. At laser fluences smaller than 1 J/cm^2, it was found that the shape of the shockwave front is far from hemispherical at the moment of the radius measurement (50 ns). [1,4]

3. I was the first to certify that the HOPG surface melts due to the irradiation by ArF laser pulses of several J/cm^2 fluence. (i) A computer program solving the heat conduction equation was used to approximate the temperature of the irradiated region. This resulted in surface temperature reaching the melting point already at 1 J/cm^2 fluence. (ii) By means of fast photography it was shown that the deformation of the irradiated graphite surface at the rim of the ablation hole is permanent above 12 J/cm^2

fluence. This was contributed to the squirting of the molten material. (iii) The existence of polycrystal regions in graphite irradiated at 2.75 J/cm^2 fluence, revealed by transmission electron microscopy was explained by resolidification of the molten phase. [2]

4. The size distribution of nanoparticles generated by ArF laser ablation of graphite was investigated as a function of laser fluence, repetition rate and the size of the irradiated spot. The followings were concluded:
At laser fluences above the ablation threshold, size distributions show two maxima on the investigated 7-133 nm range. The broad distribution with maximum at ~50 nm diameter is to be contributed to thermal ablation. The other highly populated region expands from 7 to ~15 nm. The nanoparticle concentration in this region is not very sensitive to the fluence. Moreover, small-sized nanoparticles are also generated under threshold fluence.
Above ~20 Hz laser repetition rate the ablating pulse interacts with the nanoparticles generated by the previous pulse, evaporating them partially or totally, thus decreasing the concentration of the particles in the 7–15 nm size range, and shifting the second maximum towards small sizes.
Under $2 \cdot 10^5$ μm^2 spot size the divergence of the plume becomes high, while the oversaturation decreases, thus the integrated mass of the nanoparticles does not depend linearly on the spot size for spots smaller than the above mentioned size. [3,4]

5. Nanoparticles were characterised by different analytical methods. Scanning electron microscopy revealed spherical particles which could agglomerate during deposition on a silicon target. Röntgen diffraction of polydisperse nanoparticles as well as Raman spectra of monodisperse samples show amorphous structure. The average chemical composition of the nanoparticles is $CN_{0,08}$ and the nitrogen atoms are located in sp^3 bonding, according to the XPS spectra. [3,4]

6. Calculation of the energy that generates the shockwave lead to the conclusion that there has to be a fast desorption process taking place in a maximum 10 ns time scale.
Some ejecta was even detected by fast photography above the sample surface at 7 ns after the incidence of the laser pulse maximum at 40.4 J/cm^2 fluence.
The amount of the material that is desorbed in the first 10 ns, and generates the observed shockwave was approximated first by a method based on comparison of the shockwave energy and the energy of the

desorbed species. This resulted in a ~1 nm thick desorbed layer at ~3 J/cm^2 laser fluence.

The second estimation method is usage of the energy balance in the equation describing the shockwave propagation. This can be applied over 1 J/cm^2 and gives 0.3-1.2 nm for the thickness of the layer desorbed in the 1-2.5 J/cm^2 fluence range. Considering that these approximations are based on simple models, the order-of-magnitude correspondence of their results is sufficient. [4]

7. Size distribution spectra of nanoparticles condensing above the laser irradiated graphite surface show that there exists some material removal even at fluences under the ablation threshold. The desorbed layer thickness calculated from the integrated mass of the detected nanoparticles varies between 0.5 and 1.8 nm for the 0.1-1 J/cm^2 fluence range. From the coincidence of the order of magnitude of the desorbed layer thickness needed for the small-size nanoparticle production and for shockwave generation at fluences under ablation threshold, it was concluded that the same quick desorption process is responsible for both of these phenomena.

From the two distinct maxima of the size distribution curves it was concluded that small nanoparticles are separated from large ones in time and/or space. [3,4]

8. It was shown that the fast desorption process can not be a thermal, i. e. ergodic one, since the estimation of the mass of evaporated material based on the thermal Wigner-Polányi model resulted in mass order of magnitudes less than the total mass of nanoparticles detected at 0.5 J/cm^2. [4]

Based on the above statements it can be claimed, that — since material removal above threshold, generally referred to as ablation, takes place on a 100 ns time scale and shows thermal character, while fast desorption takes place on a time scale not longer than 10 ns and is non-thermal — the ArF laser ablation of graphite is an at least two-step process, the first non-ergodic step of which results in much less material removal than the second, thermal step.

IV. PUBLICATIONS THAT THE THESES ARE BASED ON

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3. Zs. Márton, L. Landström, M. Boman, P. Heszler: „A comparative study of size distribution of nanoparticles generated by laser ablation of graphite and tungsten", Mat. Sci. Eng. C **23** 225-228 (2003)

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2. Zs. Bor, B. Hopp, Zs. Márton, Z. Gogolák, F. Ignácz: "Ultrafast photography of shock waves originating from an ablated surface" (SPIE Vol. 1983 (1993), 748)

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Oral presentations:

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2. Márton Zs., Hopp B., Tóth Zs., Csete M., Ignácz F.,Bor Zs.,: “Elmozdulás mérése nanoszekundumos feloldású stroboszkóppal”; Optikai módszerek a korszerű méréstechnikában; 1998. 02. 19., Budapest

3. Márton Zs., Hopp B., Tóth Zs., Csete M., Ignácz F.,Bor Zs.,: “Excimer lézeres abláció vizsgálata nanoszekundumos időfelbontással”; “Tavaszi szél” a fiatal magyar tudományos kutatók és doktoranduszok II. Világtalálkozója 1998. 04. 3-5., Gödöllő

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