

Summary of the Ph.D. thesis

**NANOSTRUCTURED FILMS AND INDIVIDUAL
NANOPARTICLES BY ABLATION WITH ULTRASHORT
LASER PULSES**

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INTRODUCTION

The three keywords of the thesis are thin films, nano- and laser. Thin films represent an important class of functional materials. The production, characterization and application of nanomaterials attracted much interest during the last decades. The application of lasers in materials processing dates back to the birth of the laser and the discovery of new laser types has been regularly followed by novel applications. Pulsed Laser Deposition, PLD is an extremely versatile laboratory technique intended primarily for pilot production of thin films of materials hard to handle.

Boron carbide, B_4C is the third hardest material known behind diamond and cubic boron nitride. Above $1100^\circ C$, however, boron carbide becomes the hardest one. The fabrication of boron carbide in thin film form is still a challenge. It is logical to suppose that PLD should be an appropriate technique for production of boron carbide thin films of predetermined properties, nevertheless, the results reported up to now are far not encouraging. The droplets formed during ablation with nanosecond pulses destroy the morphology of the films and the chemical composition of the films produced deviates from that of the B_4C target used regularly. Though there are indications that the appearance of droplets is detrimental not only in respect of the morphology, but their presence influences the chemical composition of the films as well, the reports available in the literature do not answer the question: what is responsible for the deviation from the stoichiometry. Though it seems to be plausible that pulse shortening and the concomitant decrease in pulse energy might increase the chance of stoichiometric transfer, I could not find any report on boron carbide film growth using pulses of femtosecond duration.

By using ultrashort pulses not only precise and clean processing of materials can be achieved, but direct production of nanoparticles, as well. In a series of papers published in the last few years S. Amoruso and coworkers convincingly demonstrated that ablation of any solid target with ultrashort pulses of intensities within the 10^{11} - 10^{13} Wcm^{-2} domain inevitably led to the generation of nanoparticles of the target material. The comparison of results obtained on ablating Si, Ni, Fe, Au, Ag, Ti and TiC with pulses of 80-900 fs duration suggests that the behaviour of the plasma represent a common, general feature of fs-ablation, and the size distribution of the nanoparticles produced is fairly similar.

The results suggest that ablation with ultrashort pulses of intensities not much higher than the plasma formation threshold, at least within the parameter window examined, is characterized by a number of general features, independently of the nature of the target

material. In particular, the (nearly) adiabatic cooling drives the material into a metastable phase, and results in the production of a relatively large fraction of nanoparticles through phase decomposition processes. The process works in a broad range of pressures even in UHV. The two key parameters are the duration and the intensity of the pulses. The experimental findings are in line with the theoretical analyses which predict that the intensity window of 10^{12} - 10^{13} Wcm^{-2} should be the best for nanoparticle production. Based on the above considerations collection of the plasma components on substrates could be a general and practical route to production of nanostructured films of different materials.

Though it has been documented that by ablating liquid targets one of the drawbacks of PLD, ie. the formation of particulates and droplets of micrometer dimension formed as a result of the erosion of the solid target can be avoided, no reports could be found on ablation of liquid targets with ultrashort pulses.

OBJECTIVES

Since the presence of droplets is one of the biggest problems hindering the more widespread application of PLD, my primary aim was to answer the question whether is it possible to grow droplet-free boron carbide films by pulse shortening or not. An inherent problem of the comparison of the results of experiments performed using nano- vs. femtosecond lasers is the orders of magnitude difference in the power densities. The sub-ps dye/excimer laser system available in the High Intensity Laser Laboratory of the Department of Experimental Physics, University of Szeged offered a unique possibility to perform comparable experiments by using pulses of the same wavelength but different duration.

The next step of the planned work was the description of the mechanism of the growth process and the properties of the films produced. In particular, the dependence of the growth rates on the laser parameters and the determination of the chemical composition and optical properties of the films. This order meant chronological order as well.

There exists a consensus within the laser community that ablation of solid targets with ultrashort pulses results in direct formation of nanoparticles. The motivation of the experiments the results of which are shown in the second part of the thesis was to find answer to the question whether the statements formulated for the case of ablation of solid targets do remain valid for the ablation of liquid targets or not. In other words: is it possible to produce nanoparticles and nanostructured films by ablating a liquid target with femtosecond pulses? The description of the properties of the nanoparticles formed as compared to those of the target material posed a further problem.

MATERIALS AND METHODS

The films were grown by PLD using a high brightness hybrid dye/excimer laser system, delivering 700 fs pulses of several tens of mJ maximum energy at 248 nm and running at max. 2 Hz. The experiments were accomplished in high vacuum. Boron carbide films were produced by ablating a hot pressed 99.5% pure B₄C target, rotating at ~1 rpm, at room temperature. The Si(100) substrates were placed parallel to the target at a distance of 40 mm. The laser beam impinged on the target at 45°. The DC-705 silicone oil was kept in a PTFE holder placed horizontally at the bottom of the chamber. Both the total pulse energy $E_t = E_{fs} + E_{ASE}$ and the contribution of the ASE, E_{ASE} were individually measured before and after each deposition run.

The morphology and the dimensions of the grains of the boron carbide films were measured by a TopoMetrix 2000 and a PSIA XE-100 AFM. The thickness profile of the films of several hundreds of nanometer thickness was determined by a DEKTAK 8 profilometer along masked steps. Rutherford backscattering spectrometry with a focused He⁺ ion beam was applied for mapping the elemental film thickness profiles at ATOMKI in Debrecen. The lateral distribution of the ¹⁰B isotope was followed by neutron radiography. 2D mapping of both the optical properties and the thickness distribution of the films was accomplished by a WOOLLAM M-2000F variable angle spectroscopic ellipsometer.

Changes in the chemical structure and the surface properties of the films produced by ablating the silicone oil with emphasis on texture and morphology on micro- and nanoscale as a function of the substrate temperature were followed by optical microscopy, FTIR, FESEM and AFM. The low magnification pictures were taken by a Nikon LABOPHOT-2A microscope. IR spectra were recorded on a Bio-Rad Digilab Division FTS-65A/896 FTIR spectrometer with the bare KCl substrates in the beam path as references. The nanoscale surface morphology of the films was characterized by a HITACHI S-4700 FESEM and a PSIA XE-100 AFM in tapping mode, while mapping of the micromechanical properties of the films was performed using a WITec GmbH DPFM AFM operating in digital pulsed force mode. The lateral size distributions and the nanostructure of the nanoparticles were derived from the analysis of TEM pictures taken by a CM20 and a JEOL 3010 microscope, respectively.

NEW SCIENTIFIC RESULTS

Boron carbide thin films by pulsed laser deposition

1. As a result of a comparative atomic force microscopy study of boron carbide thin films grown by ablating the same target with two lasers emitting at the same wavelength and delivering pulses of 25 ns and 700 fs duration, respectively, while keeping all other experimental conditions constant, I have demonstrated that the formation of droplets larger than one micrometer in diameter can be eliminated by pulse shortening [T1]. The net result is significant improvement in the surface morphology. Furthermore I have shown that, independently of the duration of the ablating pulses, the films are built up from flat nanoparticles of several tens of nanometer diameter and a few nanometer height, as determined by high resolution AFM [T1].

2.a By 2D mapping of the thickness distributions of two films deposited using laser spots of order of magnitude difference in areas, performed by spectroscopic ellipsometry, I have shown that larger spot size – with approx. one order of magnitude smaller energy density – results in a more than fourfold increase in maximum thickness and – what is directly comparable – an increase in film volume by a factor of two. An important corollary of this result is that in the case of ablation with femtosecond pulses the energy- and power density, routinely used as relevant parameters within the laser community, do not define unequivocally the film properties. In order to ensure an unambiguous assignment simultaneous definition of both the pulse energy and spot size is necessary [T1].

2.b The statement that ablation with sub-ps pulses results in much higher growth rates than those obtained when using pulses of nanosecond duration even for two orders of magnitude less energy densities is of both theoretical and practical importance [T1].

2.c By mapping the thickness distributions in two series of boron carbide films deposited systematically changing the pulse energies focused onto 0.09 and 1.02 mm² spot areas, using profilometry along masked steps of the films, I have determined the dependence of the distributions as a function of the energy of the pulses. I have shown that larger spot sizes result in bigger film volumes, when keeping the pulse energies fixed, ie. ablation using larger spot sizes is beneficial. The result that with the same energy density – depending on the actual spot size – more than one growth rate can be produced, further proved the statement that in PLD performed with ultrashort pulses the energy density alone is not appropriate for the unambiguous assignment of the growth rate to the process parameters. In pulse energy representation, however, the growth rates become comparable. As a consequence: the pulse

energy is the principal parameter, nevertheless providing simultaneously the spot size is absolutely necessary [T1].

3. I have pointed out that the effect of the ASE must inevitably be considered during experiments in materials processing performed by femtosecond laser systems. The measurement of the temporal contrast is a prerequisite to the correct evaluation and interpretation of the results. Due to the five orders of magnitude difference in pulse duration high intensity contrast does not mean necessarily high enough difference in the respective energies, the adequate parameter is the energy contrast. I have proven that the effect of a given contrast depends on the spot dimensions, as well [T2].

4. Using μ RBS I have proven that the elemental composition of boron carbide films changes continuously along the symmetry axes from boron rich in the centre to carbon rich approaching the edges [T3]. Instead of the natural $^{10}\text{B}/^{11}\text{B}$ ratio of 0.23 the relative abundance of the boron isotopes varies between ~ 0.2 and ~ 1.1 with a local maximum near to the centre of the deposit [T3], while the concentration of the ^{10}B isotope increases by a factor of three when moving from the edges to the centre [T5]. By comparing the thickness distributions and the respective changes in chemical composition I have calculated the density values as a function of the lateral position along the symmetry axes. I have shown that the density monotonously increases from the edge to the centre, nevertheless it remains well below that of the bulk B_4C [T4].

5. The optical properties of the films show similar behaviour. The $k(\lambda)$ and $n(\lambda)$ curves shift to lower values when moving outwards from the centre. The E_{04} optical bandgaps vary between ~ 3.2 and ~ 4 eV depending on the actual lateral position, reaching a minimum value in the centre of the film and increasing when moving toward the edges. The refractive index measured at 633 nm reaches a value of ~ 1.61 in the centre with a monotonous decrease down to ~ 1.52 when moving 16 mm away, indicating increasing porosity, ie. loosening in the structure. The results obtained by ellipsometry are in perfect agreement with those referring to the chemical composition: when moving outwards, the composition changes from B_3C to $\text{B}_{0.6}\text{C}$ with a concomitant decrease in mass density from ~ 1.2 to ~ 0.6 gcm^{-3} [T4].

Nanostructured films and individual nanoparticles by pulsed laser deposition

6.a I have demonstrated for the first time that ablation of a liquid target with ultrashort pulses results in direct formation of nanoparticles. By ablating a silicone oil with extremely clean sub-ps pulses in high vacuum I have deposited nanostructured films consisting of

C:Si,H,O nanoparticles of less than 100 nm diameter with relatively narrow size distribution, as the main component [T6].

6.b By evaluating pictures taken on films of less than one monolayer thickness by atomic force- and transmission electron microscopy I have demonstrated that the dimensions of the C:Si,H,O nanoparticles produced by pulses of 700 fs duration in vacuum increases with increasing number of pulses. By ablating with one and eight pulses the mean size of the heights and the diameters increases from 1.07 to 3.89 nm and from 9 to 27 nm, respectively. The total volume of the nanoparticles increases linearly with the pulse number, while their number shows different dependence, which most probably points to the contribution of surface effects, eg. coalescence. The nanoparticles possess partially ordered amorphous structure with cubic SiC and Si(111) nanocrystals embedded into an amorphous hydrogenated carbon matrix [T7].

PUBLICATIONS IN PEER REVIEWED JOURNALS RELATED TO THE THESIS

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