STUDY ON MATERIAL REMOVAL FOR THE PURPOSE OF REDUCTION OF THE PARTICULATE GENERATION DURING PULSED LASER DEPOSITION

PhD thesis

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1. Introduction

When a high power laser beam is focused onto a target surface, a hot material cloud (plume) is emitted from the surface as the consequence of the irradiation. The plume can be deposited in the form of a thin film onto a substrate placed above the ablated area. This conceptually simple method is called pulsed laser deposition (PLD). The experimental setup generally consists of a target holder and a substrate holder placed in a vacuum chamber. The processes usually take place in vacuum, however film growth can be carried out in a reactive environment, too. Because of the lack active electrical elements, such as filaments and discharge electrodes, many kind of reactive gas can be used. Another advantage of the PLD is the high reactivity of the ablated species due to their electronic excitation. In contrast with the simplicity of the experimental setup, the laser-matter interaction is a very complex process which depends on the parameters of the laser (wavelength, fluence, pulse length) as well as on the optical, thermodynamical properties and topography of the target. The absorbed laser energy fist converts into excitation energy of the electrons after that into chemical, thermal and mechanical energy, causing the material removal. The ablated plume consists of a mixture of atoms, molecules, ions, micrometer sized solid particulates and molten droplets. As a result of the high pressure inside the plume, it expands rapidly with narrow forward angular distribution.

The advantages of this method are that the average stoichiometry of the deposited material can be preserved (if desired) during the PLD when appropriate deposition parameters are used, the energetic evaporants make possible growth of compact thin layers, and the thickness of the films can be well controlled. The disadvantages of the procedure are the presence of the micron-sized particulates on the deposited films and the narrow forward angular distribution of the plume that makes difficult the large-area deposition.

For generation of micrometer sized particulates several processes are responsible. The structures existing on the intact surface or created during the repeated ablation can be easily broken by the thermal shock induced during the laser irradiation. The subsurface boiling, which occurs if the time required to transfer laser energy into heat is shorter than the time needed to evaporate a surface layer with a thickness on the order of skin depth, expels micron-sized droplets. Under this condition, the subsurface layer is superheated before the surface itself has reached the vapor phase. The strong recoil pressure of the evaporated material onto the liquid target or liquid layer formed on the irradiated area also contributes to droplet generation. Up to now many attempts were made to improve the film morphology by reducing the deposited micron-sized particulates, however they could not be completely eliminated.

2. Aims

Since more detailed knowledge about the influence of the ablation parameters on the particulate generation could contribute to the improvement of the quality of the thin layers made by PLD, the aims of my work can be summarized as follows:

- I intended to study the influence of the target morphology on particulate generation during excimer laser ablation of polytetrafluoroethylene.
- By using molten targets (if it is possible) the formation of solid particulates can be avoided, however the splashing effect becomes significant. Therefore my goal was to investigate the material ejection during ablation of two molten metals (tin and bismuth) having different thermal and mechanical properties.

- The viscosity of the liquid targets is supposed to influences the particulate generation due to its effect on the flow. My aim was to study how, and in which degree the viscosity influences the droplet generation during laser ablation.
- The velocity of the atomic and molecular species of the ablated plume important for laser deposition is with about two orders of magnitude higher than those of micrometer sized particulates. Therefore I intended to investigate in which degree the different sized particulates can be spatially separated when using rotational target holder.

3. Experimental methods

During my experiments an ArF excimer laser having 193 nm wavelength and 20 ns pulse length was used for ablation of different targets. The material ejection was studied with the following methods.

Determination of the dimension and number of the micrometer sized particulates emitted during laser ablation

The particulates ejected during to the irradiation with a single laser pulse were collected on a quartz plate placed above the target surface. The deposited particulates were observed through an optical microscope and the images were recorded by a video camera. The number and the size of the particulates were determined either by computer software, or manually, depending on which method was the advantageous one. The volume of the deposited droplets was determined assuming hemispherical shape.

Time-resolved investigation on the material ejection

The process of the material removal could be followed with help of a fast photographic arrangement. The target was illuminated by Coumarin 153 dye laser pulses having 1 ns length which were delayed electronically compared to the ablating excimer pulses. The exposed contour of the target surface was observed by a microscope-camera system.

Spatial separation of fast and slow components of the ablated plume

The target was placed onto a rotating holder and the excimer laser beam was focused as a line close to the edge of the target with a cylindrical lens. The maximum obtainable circumferential velocity of the ablated area was 36.4 m/s. When the target is rotated the ejected particulates obtain a velocity component parallel with the surface. This leads to a slight (negligible) modification of the angular distribution of the high velocity atoms and molecular particles, while the angular distribution of the slower, micrometer sized particulates, shifts towards the direction of the target velocity vector and this may result in spatial separation.

4. New scientific results

1. The influence of the target morphology on the material ejectionl during excimer laser ablation of polytetrafluoroethylene was studied.

1.a It was shown that during the ablation of the same area with several pulses the treated surface became severely damaged and sponge-like structures were developed, which can be easily removed by further laser irradiation from the surface [1].

1.b It was demonstrated that the particulate generation strongly depends on the morphology of the target surface, the rougher surface results in higher number of ejected particulates. In the case of the ablated PTFE the particulate generation was found to depend on the microscopic roughness (structures with the size of several micrometers) of the surface. The generation of the undesirable particulates during excimer laser ablation can be reduced by the use of targets having smooth surface [1].

2. The process of the material ejection during laser ablation of molten tin and bismuth was investigated.

2.a The events could be followed in two characteristic time domains: emission of the ablated plume in nanosecond time domain, and emission of micrometer sized particulates and surface wave development microsecond range [2].

2.b It was proved that the number and the size of the droplets depended on the applied laser fluence and the properties of the targets. The surface of the bismuth was more sensible to the effect of the laser pulse than that of tin. This can be attributed to the followings: at given fluence the momentum of the plume is higher in the case of bismuth than in the case of thin and also bismuth has lower viscosity and surface tension [2].

3. The influence of the state of matter and the viscosity on the ablation in ambient air of polyethylene-glycol 1000 was studied.

3.a It was demonstrated that the plasma development and the properties of the shock wave did not depend on the state of the target [3].

3.b My experiments showed that in the case of solid PEG 1000 intense particulate generation takes place. Increasing the temperature of the sample slightly above the melting point the number of the particulates decreased by two orders of magnitude and their maximum size by a factor of five [4].

3.c Increasing the viscosity of the molten PEG from 0.04 Pa·s to 0.14 Pa·s the droplet number decreased by a factor of 10, while the total volume of droplets decreased by approximately three orders of magnitude. The lowest particulate number was found at target temperature close to the melting point [4].

3.d It was proved that, although the PEG 1000 was only a model material, the particulate generation can be reduced when using molten target and keeping its viscosity at the highest possible value (close to the melting point) [4].

4. The efficiency of spatial separation of fast and slow components of the ablation plume as the function of the circumferential velocity of the rotating target was studied in the case of Polyethylene-glycol 1000. Previous fast photographic measurements showed that the velocity of the molecular and micrometer sized particulates were 8700 m/s and 30 m/s, respectively.

4.a Regarding the rotational direction as positive, in the case of standing target the flow angle of the particulates compared to the normal of the surface was between ±65^{o}. Increasing the rotational velocity, the angular distribution of the droplets shifted toward positive values. At 36.4 m/s velocity the smallest value of the flow direction was about -10^{o}, what means that during PLD practically one half of the deposition are is practically free of particulates [5].

4.b It was demonstrated that using rotational target holder with adequate circumferential velocity, the micrometer sized particulates can be separated from the smaller (approximately nanometer sized) constituents of the ablation plume, making possible the deposition of smoother thin layers [5].

5. Publications constituting the basis of the thesis

1 T. Smausz, N. Kresz, B. Hopp: *Target morphology dependence of the particulate generation during excimer laser ablation of polytetrafluoroethylene*, Appl. Surf. Sci. **177**, 66-72 (2001)

2 Zs. Tóth, B. Hopp, T. Smausz, Z. Kántor, F. Ignácz, T. Szörényi, Zs. Bor: *Excimer laser ablation of molten metals as followed by ultrafast photography*, Appl. Surf. Sci. **138-139**, 130-134 (1999)

3 B. Hopp, T. Smausz, E. Tombácz, T. Wittmann, F. Ignácz: *Solid state and liquid ablation of polyethylene-glycol 1000: temperature dependence*, Opt. Com. **181**, 337-343 (2000)

4 T. Smausz, B. Hopp, Cs. Vass, Z. Tóth: *Experimental study on droplet generation during excimer laser ablation of polyethylene glycol 1000*, Appl. Surf. Sci. **168**, 146-149 (2000)

5 B. Hopp, N. Kresz, Cs. Vass, Z. Tóth, T. Smausz, F. Ignácz: *Spatial separation of fast and slow components of pulsed laser plumes*, Appl. Surf. Sci. **186**, 298-302 (2002)